

THESIS FOR THE DEGREE OF
PHILOSOPHÆ DOCTOR

Ample Rare Elements

A Geochemical Anomaly in the
Earth's Crust at Norra Kärr

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Cover: Peralkaline pegmatoid vein with red eudialyte crystals, which are rich in rare-earth elements, displaying a cross-cutting relationship with the peralkaline nepheline syenite host rock. Photo: Magnus Leijd.

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To Loke and Nora.

Abstract

The Norra Kärr alkaline complex in southern Sweden (58°06'N, 14°34'E) is a classic occurrence of agpaitic rocks, which contains a large mineral deposit of rare-earth elements (REE), Zr, and Nb. The complex consists of different varieties of agpaitic peralkaline nepheline syenite that are defined by the occurrence of Na-rich Zr–Ti silicate minerals that contain volatiles F and Cl, including members of the rinkite, catapleiite, and eudialyte groups. The eudialyte-group minerals in Norra Kärr contain different ratios of light to heavy REE across the lithological domains.

The magmatic age of the alkaline complex, which is poor in common chronometric minerals, was determined at 1.49 ± 0.01 Ga (2σ) by U–Pb dating of zircon that formed during alkali metasomatism (finitisation) of the surrounding 1.8 Ga granite. The $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratio of this metasomatic zircon is different from Hf isotopes in the granite, but is identical with the Hf isotope composition of Lu-poor eudialyte from the alkaline complex. The relatively highly radiogenic composition of the Hf isotopes is consistent with a mantle source for the agpaitic magma.

New radiometric dating methods were developed. These allow precise *in situ* measurements of isotope ratios of the Rb–Sr and K–Ca as well as Sm–Nd systems in K-rich and Nd-rich minerals, respectively. Three varieties of alkaline rocks in Sweden were dated by the *in situ* Rb–Sr method. Biotite Rb–Sr cooling ages in the region east of Norra Kärr are approximately coeval with the emplacement of the alkaline rocks.

The complex has been affected by metamorphic overprinting. The foliated and folded fine-grained nepheline syenite is frequently cross-cut by coarse-grained eudialyte-rich pegmatoids. One eudialyte crystal with primary zoning from a pegmatoid was pre-characterised by SEM BSE imaging and *in situ* chemical analysis by LA-ICP-MS, including full REE composition and precise Sm/Nd ratios. Sampling at a resolution of <200 μm by micromill provided a sufficient Nd aliquot for routine high-precision ID-TIMS Sm–Nd isotope analysis. Eudialyte crystal growth was dated at 1144 ± 53 Ma (2σ) in the undeformed pegmatoid vein, about 350 million years after the magmatic event. The pegmatoid is suggested to have formed by low-temperature partial melting of the peralkaline nepheline syenite host at the margin of Sveconorwegian orogeny.

The agpaitic rocks were produced from a magma that formed by extensive fractional crystallisation of an alkali basaltic parental magma. The concentrations of highly enriched incompatible elements in the most differentiated nepheline syenite may indicate 98 % crystallisation of the parental magma.

Keywords: rare-earth elements; eudialyte; geochemistry; geochronology; ore geology

Sammanfattning

Norra Kärr alkalina komplex i södra Sverige (58°06'N, 14°34'E) är en klassisk förekomst av agpaitiska bergarter, vilken innehåller en stor mineralförekomst av sällsynta jordartsmetaller (REE), Zr och Nb. Komplexet består av olika varieteter av agpaitisk nefelinsyenit vilka definieras av förekomsten av Na-rika Zr-Ti silikatmineral med volatila ämnen F och Cl, inkluderande rinkit-, katapleit- och eudialytgruppens mineral. Eudialytgruppens mineral i Norra Kärr innehåller lätta och tunga REE i olika förhållanden mellan de olika bergartsdomänerna.

Den magmatiska åldern för det alkalina komplexet, som är fattigt på vanliga kronometriska mineral, bestämdes till $1,49 \pm 0,01$ Ga (2σ) genom U-Pb-datering av zirkon som bildades vid alkalin metasomatos (fenitisering) av den omgivande 1,8 Ga graniten. Isotopkvoten $^{176}\text{Hf}/^{177}\text{Hf}$ i denna metasomatiska zirkon skiljer sig från Hf-isotoper i graniten, men är identisk med Hf-isotoper i Lu-fattig eudialyt från det alkalina komplexet. Den förhållandevis höga radiogena sammansättningen av Hf-isotoperna är förenlig med ett mantelursprung för den agpaitiska magman.

Nya radiometriska dateringsmetoder har utvecklats. Dessa möjliggör noggranna in-situ-mätningar av isotopkvoter av Rb-Sr och K-Ca samt Sm-Nd i K-rika respektive Nd-rika mineral. Tre varieteter av alkalina bergarter i Sverige har daterats med in-situ Rb-Sr-datering. Biotit Rb-Sr avsvalningsåldrar i området öster om Norra Kärr är ungefär samtida med de alkalina bergarternas uppkomst.

Komplexet har utsatts för metamorf omvandling. Den folierade och veckade finkorniga nefelinsyeniten är genomsatt av klippande grovkorniga eudialytiska pegmatoïder. En eudialytkristall med primär zonering från en pegmatoïd förkarakteriserades med SEM BSE-avbildning och in-situ kemisk analys med LA-ICP-MS, inklusive alla REE och noggranna Sm/Nd-kvoter. Provtagning med <200 μm upplösning med mikroborr förskaffade en tillräcklig Nd-alikvot för rutinmässig högnoggrann ID-TIMS Sm-Nd isotopanalys. Eudialyttillväxt daterades till 1144 ± 53 Ma (2σ) i den klippande pegmatoïdådern, cirka 350 miljoner år efter den magmatiska händelsen. Pegmatoïden föreslås ha bildats vid lågtemperatur partiell uppsmältning av den peralkalina nefelinsyeniten nära fronten på den svekonorvegiska orogesen.

De agpaitiska bergarterna kristalliserade ur en magma som bildades genom långtgående fraktioneringskristallisation av en alkalibasaltisk modermagma. Koncentrationerna av höganrikade inkompatibla ämnen i den mest differentierade nefelinsyeniten kan tyda på 98 % kristallisation av modermagman.

Keywords: sällsynta jordartsmetaller; eudialyt; geokemi; geokronologi; malmgeologi

Popular science summary

Rare-earth elements fill an important role in the technology of today, including in mobile phones, robotics, low-energy lighting, and medical equipment. They are especially important to the renewable energy transition, because they are used in large quantities in wind turbines, solar panels, batteries, and electric motors. The demand for these metals in Europe is expected to more than double until 2030 solely from the increased use of renewable energy and e-mobility.

The global supply of rare-earth elements is dominated by Chinese production. Especially in Europe we are completely dependent on import of Chinese raw materials, since we lack a production chain of our own for these metals. The production of rare-earth elements in China is coupled with large environmental problems and risks for public health. Moreover, China has enforced stringent export restrictions. The tangible risk for a supply shortage combined with the large economic importance of these metals has led to their current classification as the most critical raw materials in the EU.

Norra Kärr is a large geological deposit of rare-earth elements in Sweden north of Gränna, on the border between the counties of Jönköping and Östergötland, which from a geological point of view has the potential to become an important resource for the EU. The rock types found here do not occur anywhere else in Sweden and consist of exotic minerals with an anomalous chemical composition compared to most other rocks in the Earth's crust.

My research has contributed to an increased understanding of the distribution of rare-earth elements between different minerals and rocks in Norra Kärr. In particular I focussed on the chemical composition of the mineral eudialyte, which is the main host for the rare-earth elements.

Through the development of new methods for the precise age determination of the minerals and rocks, I have managed to gather new insights into the rocks' origin and formation in relation to ancient tectonic processes. The rocks originated from a magma that formed in the mantle deep beneath the Earth's crust, which became enriched in rare elements through slow crystallisation and subsequently intruded the Småland granite at one and a half billion years ago. One billion years ago, when the Swedish west coast featured a Himalaya-like mountain range, the rocks in Norra Kärr were affected by mountain-building pressures and elevated temperatures, which caused the rocks to partially melt again. This has affected the rocks' shape and appearance and how the rare-earth elements are distributed within them.

Populärvetenskaplig sammanfattning

Sällsynta jordartsmetaller fyller en viktig funktion i dagens teknik, i allt från mobiltelefoner till robotar, lågenergilampor och sjukhusinstrument. De är särskilt viktiga i den gröna energiomställningen, eftersom de används i stora mängder i bland annat vindkraftverk, solceller, batterier och elmotorer. Efterfrågan på metallerna i Europa väntas kunna mer än dubbla till år 2030 enbart från den ökade användningen av förnybar energi och elfordon.

Det globala utbudet av sällsynta jordartsmetaller domineras av kinesisk produktion. Särskilt i Europa är vi helt beroende av importen av kinesiska råvaror, eftersom vi saknar en egen produktionskedja för dessa metaller. I Kina är produktionen av sällsynta jordartsmetaller förknippad med stora miljöproblem och risker för folkhälsan. Kina har dessutom infört hårda exportrestriktioner. Den påtagliga risken för ett tillförselunderskott i kombination med metallernas stora ekonomiska viktighet för samhället har lett till att de i dagsläget klassas som de mest kritiska råvarorna i EU.

Norra Kärr är en stor geologisk fyndighet av sällsynta jordartsmetaller i Sverige norr om Gränna, på gränsen mellan Jönköpings och Östergötlands län, som från ett geologiskt perspektiv har potentialen att bli en strategisk resurs för EU. Bergarterna som finns här förekommer ingen annanstans i Sverige och består av exotiska mineral som har en anomal kemisk sammansättning jämfört med de flesta bergarterna i jordskorpan.

Min forskning har bidragit till en ökad kännedom om fördelningen av sällsynta jordartsmetaller mellan olika mineral och bergarter i Norra Kärr. I synnerhet fokuserade jag på den kemiska sammansättningen av mineralet eudialyt, vilket är den huvudsakliga avsättningen för de sällsynta jordartsmetallerna.

Genom att utveckla nya metoder för att noggrant kunna åldersbestämma mineralen och bergarterna har jag kunnat förskaffa nya insikter i bergarternas ursprung och bildande i relation till urgamla tektoniska processer. Bergarterna fick sitt ursprung ur en magma som bildades i jordmanteln djupt nere under jordskorpan, som genom långsam kristallisation anrikades på sällsynta ämnen och sedan trängde in i den småländska graniten för en och en halv miljard år sedan. För en miljard år sedan, när Västkusten präglades av en Himalaya-liknande bergskedja, påverkades bergarterna i Norra Kärr av bergskedjetryck och förhöjda temperaturer, som orsakade att berget delvis smälte upp igen. Detta har påverkat bergarternas form och utseende och hur de sällsynta jordartsmetallerna är fördelade.

Preface

This is the work that constitutes my dissertation for the degree of *Philosophiæ Doctor* in Natural Science, specialising in Geology, at the University of Gothenburg.

In the Spring of 2011, I looked at fresh drill cores in a barn in Kaxtorp, located on the border to the exotic rocks in Norra Kärr. Since then, with variable degrees of activity, I have researched and written about this topic. The project was originally intended for my Master of Science thesis, but, fuelled by my fascination with the agpaaitic rocks and a desire to work on a PhD, it outgrew its original scope. My time as a part-time doctoral student officially started in May 2015. Although I tried hard to be an eternal student, my work has now finally amalgamated into this doctoral dissertation.

My first expressions of gratitude go out to my current and former advisors Thomas Zack, Johan Hogmalm, and David Cornell, who have challenged me from time to time while also giving me full support and the creative liberty to operate without strict bounds. My mentor Tom Andersen has been an invaluable source of knowledge and expertise since the project's conception. Examiners Erik Sturkell and Rodney Stevens have provided valuable support and direction to the project.

The PhD project was largely funded by the Geological Survey of Sweden (SGU). I have received great support and insights by its staff, especially Lena Lundqvist and Thomas Eliasson, who have always welcomed me and provided me with generous amounts of service and discussion.

Working as a geologist for Tasman Metals in Gränna in the Summer of 2012 gave me an intimate familiarity with the ins and outs of the rocks in Norra Kärr, which has been more than beneficial to my research. I wish to thank my former colleagues for a great Summer in Gränna and interactions since then, in particular Magnus Leijd, Johan Berg, Henning Holmström, Mark Saxon, Glenn Patriksson, Stina Ranjer, and Andrew Bradley. Britt Bluemel also should be mentioned here, who won our competition by publishing her first scientific article in 2013 just before I did. Petya Atanasova worked simultaneously and in parallel on her PhD thesis focussing on other aspects of Norra Kärr (defended in 2020); I have greatly enjoyed our annual discussions at the departure gate in Toronto.

I want to thank all current staff and PhD students at the Department of Earth Sciences for a nice work environment. Former staff who deserve a special mention are Kerstin Ericson, Lennart Björklund, Sven Åke Larson, Eva-Lena Tullborg, Rob Hellingwerf, Stefan Banzhaf, Mattias Ek, Linus Brander, Karin Appelquist, Eric Hegardt, Henrik Drake, Martin Persson, Valby van Schijndel, Ardo Robijn, Ezra Haaf, April Shannon, and my office mates Mikael Tillberg and Aifang Chen.

Throughout the duration of the project, I have suggested topics for and helped supervise Bachelor and Master of Science thesis projects for Ulf Christensson, Stina Ranjer, Dario Partalo, Erik Kangas, Andreas Eriksson, John Eliasson, and Adi Fazic. In return, their work has contributed directly or indirectly to my own research and knowledge, which I want to acknowledge here.

Researchers who have supported me, answered my strange questions, and helped me along in some fashion include Ulf Bertil Andersson, Michael Marks, Erik Jonsson, Karin Högdahl, Dan Holtstam, Jörgen Langhof, Andreas Karlsson, Ellen Kooijman, Matthijs Smit, Ethan Baxter, Denise Honn, Gabrielle Stockmann, Paula Lindgren, Thomas Lundqvist, David Dolejš, Sergey Aksenov, Aniket Chakrabarty, Henrik Friis, and Adrian Finch. Jan Lundqvist and Jan-Olov Svedlund are thanked for a great introduction to the Särna alkaline rocks in the Summer of 2013.

Young researchers I have had the pleasure of meeting, now and then, in different parts of the world to discuss strange rocks include Stefan Andersson, Anouk Borst, Quinten van der Meer, Sam Broom-Fendley, Emma Hunt, Jeremy Woodard, and Alex Leich.

My former colleagues at Minalyze in Sweden and Australia were a large and slightly crazy part of my life 2012–2019. This job gave me a chance to exercise my geological wits and brought me to interesting parts of the world with ambitious people.

Göran Svensson repeatedly invited me to speak about Norra Kärr, which finally led to a talk for the Gothenburg division the Swedish Chemical Society in 2017. This was closely followed by a talk at the Critical Raw Materials seminars in Uppsala by invitation of Erik Jonsson. Alf Olaf Larsen kindly invited me as a speaker at Norsk Mineralsymposium 2020 in Norway, which unfortunately had to be cancelled due to COVID-19 restrictions.

I thank friends and family. This work would not be what it is without their support.

The period of my life since the Spring of 2011 not only contains my research about Norra Kärr, but also the story of being in love, moving in together, getting engaged and eventually married, buying a homestead in the countryside, raising animals and two fantastic children. From time to time, you three have been the largest distraction that hindered me from working productively on this thesis, which I am ultimately very grateful for. I look forward to spending more time with you now.

And, finally, a big thank you and apology to all others, whom I have failed to mention.

Nunc est bibendum!

AxS

The first part of this thesis consists of a summary of the scientific background, a rationale and summary of the scientific papers included in this thesis, and a synthesis.

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The second part consists of these five peer-reviewed scientific articles, which are appended to the thesis.

Part Two

Paper I.

Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Erambert, M., Ek, M., Leijed, M., 2013. Three Compositional Varieties of Rare-Earth Element Ore: Eudialyte-Group Minerals from the Norra Kärr Alkaline Complex, Southern Sweden. *Minerals*, **3**, 94–120.

Paper II.

Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Christensson, U.I., Berg, J.T., 2017. Magmatic age of rare-earth element and zirconium mineralisation at the Norra Kärr alkaline complex, southern Sweden, determined by U–Pb and Lu–Hf isotope analyses of metasomatic zircon and eudialyte. *Lithos*, **294**, 73–86.

Paper III.

Sjöqvist, A.S.L., Zack, T., Honn, D.K., Baxter, E.F., 2020. Modification of a rare-earth element deposit by low-temperature partial melting during metamorphic overprinting: Norra Kärr alkaline complex, southern Sweden. *Chemical Geology*, **545**, 119640.

Paper IV.

Hogmalm, K.J., Zack, T., Karlsson, A.K.-O., **Sjöqvist, A.S.L.**, Garbe-Schönberg, D., 2017. *In situ* Rb–Sr and K–Ca dating by LA-ICP-MS/MS: an evaluation of N₂O and SF₆ as reaction gases. *Journal of Analytical Atomic Spectrometry*, **32**, 305–313.

Paper V.

Sjöqvist, A.S.L., 2019. The Tale of Greenlandite: Commemorating the Two-Hundredth Anniversary of Eudialyte (1819–2019). *Minerals*, **9**, 497.

Relevant publications

Below is a selection of relevant work presented and published during my doctoral studies that is not included in this thesis, but which provides an additional context to the contents of this dissertation.

Dissertations

Sjöqvist, A.S.L., 2015. Agpaitic Rocks of the Norra Kärr Alkaline Complex: Chemistry, Origin, and Age of Eudialyte-hosted Zirconium and Rare-earth Element Ore (Ph.Lic. thesis A157). University of Gothenburg.

Conference contributions

Sjöqvist, A.S.L., Leijd, M., Jonsson, E., Andersson, U.B., 2013. The Norra Kärr REE-Zr project. *12th Biennial SGA Meeting Excursion Guidebook: SWE3. The Norra Kärr REE-Zr project and the birthplace of light REEs. Uppsala, Sweden, 12–15 August 2013.*

Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Andersson, U.B., Christensson, U.I., Ranjer, S.J.E., Holtstam, D., Leijd, M., 2014. Geochronology of the Norra Kärr alkaline complex, southern Sweden. *31st Nordic Geological Winter Meeting, Lund, Sweden.* [Abstract, poster, and talk.]

Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Christensson, U.I., Berg, J.T., 2016. Magmatic age of the Norra Kärr alkaline complex determined by U–Pb and Lu–Hf isotopes of metasomatic zircon in fenite. *32nd Nordic Geological Winter Meeting, Helsinki, Finland.* [Abstract and talk.]

Sjöqvist, A.S.L., Zack, T., Baxter, E.F., Honn, D.K., 2016. Evidence for post-magmatic rare-earth mobilisation from a microgeochemical *in situ* ID–TIMS Sm–Nd isochron from a single magmatic eudialyte crystal from the Norra Kärr alkaline complex. *35th International Geological Congress, Cape Town, South Africa.* [Abstract and talk.]

Sjöqvist, A.S.L., Zack, T., Högmark, K.J., Kangas, E., 2018. In tandem K–Ca and Rb–Sr dating of potassic minerals by LA-ICP-MS/MS: Method and prospective applications. *33rd Nordic Geological Winter Meeting, Copenhagen, Denmark.* [Abstract and talk.]

Technical reports

ERECON, 2015. *Strengthening the European Rare Earths Supply-Chain: Challenges and Policy Options.* Kooroshy, J., Tiess, G., Tukker, A., Walton, A. (eds.).

Student theses co-supervised or advised

- Christensson, U., 2013. Characterising the Alteration of the Contact to the Norra Kärr Alkaline Complex, Southern Sweden (B.Sc. thesis B734). University of Gothenburg.
- Ranjer, S., 2013. Describing and Characterising the Mylonites in the Area of the Norra Kärr Alkaline Complex, Southern Sweden (B.Sc. thesis). University of Gothenburg.
- Partalo, D., 2015. Evaluation of innovative X-ray fluorescent scanning method for exploration purposes on a Kiruna-type apatite-iron oxide mineralization from Malmberget, Sweden (M.Sc. thesis). University of Gothenburg.
- Ranjer, S., 2016. *In situ* Rb–Sr dating of alnöite from Alnö, Sweden (M.Sc. thesis). University of Gothenburg.
- Eriksson, A., 2016. Amphiboles of the Norra Kärr alkaline complex: eckermannite, fluoro-leakeite, and elusive lithium (B.Sc. thesis B922). University of Gothenburg.
- Kangas, E., 2017. A method for quantitative determination of mean atomic number from backscattered electron images, a mineralogical focus (B.Sc. thesis B959). University of Gothenburg.
- Eliasson, J., 2018. Investigation of the Särna alkaline complex in Dalarna, Sweden (M.Sc. thesis B1019). University of Gothenburg.
- Kangas, E., 2018. Strategies for standardization and calibration of in-situ K–Ca dating by LA-ICP-MS (M.Sc. thesis B1041). University of Gothenburg.
- Fazic, A. (2018). *In situ* Rb-Sr thermochronology in southeastern Sweden (M.Sc. thesis B1037). University of Gothenburg.

Outreach

This section summarises my efforts to communicate my scientific results to a wider audience and to inform the general public about the science of geology.

Popular scientific articles

Sjöqvist, A., 2014. Sällsyntare än en lottovinst. *Geologiskt Forum*, **21**(4), 17–19.

Sturkell, E., **Sjöqvist, A.**, Björklund, L., Johnsson, A., 2015. Rock Stars: Geologists on the Silver Screen. *Earth*, **60**(5-6), 72–81.

Sjöqvist, A.S.L., 2020. Om Norra Kärr alkalina intrusions ursprung och utveckling. In *Norsk mineralsymposium 2020*, Larsen, A.O., Kjærnet, T. (eds.), Atles trykkeri AS, Stathelle. 36–43.

Sjöqvist, A.S.L., 2020. Sagan om grönlandit: eudialytens upptäcktshistoria. In *Norsk mineralsymposium 2020*, Larsen, A.O., Kjærnet, T. (eds.), Atles trykkeri AS, Stathelle. 44–52.

Interviews

“Hallå där geolog Axel Sjöqvist...” Interview for press release by the Natural Science Faculty following the release of the technical report by the ERECON, 1 July 2015.

Interviewed on local radio “Morgon i P4 Göteborg” about rare-earth elements after the release of the technical report by the ERECON, P4 Göteborg, 8 July 2015.

Invited talks

“Mineraliseringen av de sällsynta jordartsmetallerna i Norra Kärr”, presented to the Gothenburg division of the Swedish Chemical Society. Göteborg, 27 November 2017.

“Zr-REE mineralisation in the agpaitic nepheline syenites of the Norra Kärr alkaline complex”, presented at a symposium on critical metals hosted by Geological Survey of Sweden, University of Uppsala, and Swedish Mineralogical Society. Uppsala, 1 December 2017.

“

*I may not have gone where I intended to go,
but I think I have ended up where I needed to be.”*

—Douglas Adams

“

The Middle East has oil. China has rare earths.”

—Paramount leader Deng Xiaoping (1992)

1

Rare Rocks and Rare Elements

MODERN SOCIETY IS dependent on a reliable supply of raw materials that are extracted from the ground, such as iron, aluminium, and copper. The extraction and supply of raw materials are cornerstones for our economy, industry, and everyday life. With advancing technological development, society demands increasing amounts of less common metals, such as cobalt, indium, and rare-earth elements (REE; abbreviations and units are listed in Appendix I). Rare elements are increasingly incorporated in technologies that provide society with for example sustainable energy, combustion-free modes of transportation, and quality of life. Some of these rare elements, such as beryllium, zirconium, niobium, hafnium, and REE, are found in ample quantities in different varieties of alkaline igneous rocks.

1.1 Rare-earth elements

The rare-earth elements are a group of 17 chemical elements (Figure 1) that consists primarily of the 15 lanthanoids (La–Lu) and yttrium, which is chemically similar to holmium. Scandium is commonly also regarded as a REE, but is chemically distinct due to its smaller ionic radius and thus thrives in other geological environments. This clan of elements, more so than any other, leaves chemical imprints that tell scientists about the processes that formed the rocks found at the Earth’s surface and what their

H																			He
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	89-103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og		

Lanthanoids	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1. The periodic table of elements with rare-earth elements shaded grey.

ages are, the sources and development of the Earth’s crust and mantle, and the origin of the Sun and the supernovae that preceded the formation of our solar system (Cornell, 1993).

The rare-earth elements are arguably a group of “Swedish” elements, since more than half of them were first discovered by Swedish(–Finnish) chemists in minerals from two Swedish localities. The first is the mineral gadolinite, discovered in 1787 at the Ytterby pegmatite quarry in the Stockholm archipelago (Geijer, 1788), from which an oxide of the heavy rare-earth elements¹ (HREE: Y, Eu–Lu) was extracted and named “yttria” (Gadolin, 1794). The original yttria from Ytterby consisted of a mixture of chemically similar elements, from which yttrium, ytterbium, erbium, terbium, scandium, holmium, and thulium eventually would be separated.

The other is the mineral cerite from Bastnäs, near Riddarhyttan in the Bergslagen region, in which the oxide “ceria” was discovered (Hisinger and Berzelius, 1804). Notably, Klaproth independently and simultaneously also found the same element from Bastnäs, which he called “ochroïte” (Klaproth, 1804). Similarly to yttria, the original ceria consisted of a mixture of light rare-earth elements (LREE: La–Sm), from which subsequently lanthana and “didymia”, which was still a mixture of LREE, were separated (Mosander, 1844). Since the REE are so similar to each other, it took more

¹ There is no consensus in the scientific literature on the exact division between light and heavy rare-earth elements. In this thesis, the LREE consist of La, Ce, Pr, Nd, Pm, and Sm, while the HREE consist of Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. Scandium is not included in either of these subgroups.

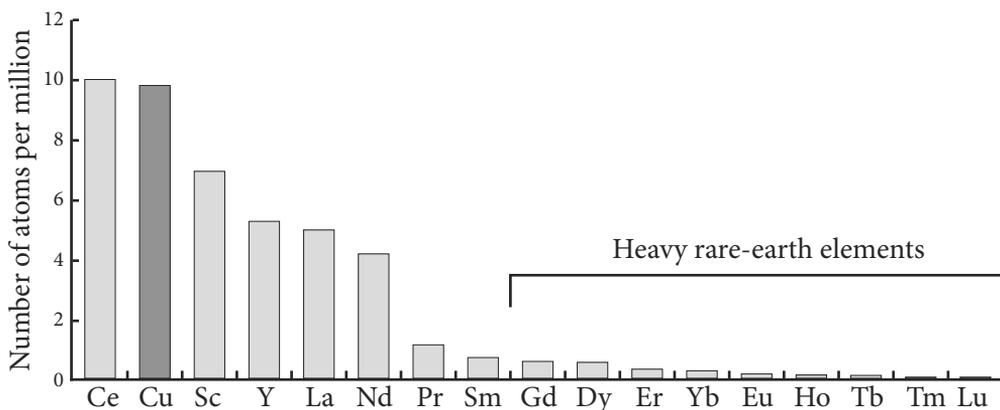


Figure 2. Atomic abundances per million atoms in the Earth's upper continental crust of copper and the rare-earth elements (Rudnick, 2005).

than a century, and many false new discoveries, before they were all finally untangled. A comprehensive account of the dramatic events surrounding the discovery of the rare-earth elements has been recalled in *Episodes from the History of the Rare Earth Elements* (Evans, 1996) and summarised in a special issue of *Elements* (Williams-Jones *et al.*, 2012).

Rare-earth elements, despite their name, are as a group relatively abundant in the Earth's crust. The composition of the Earth's crust is estimated according to different methodologies, which give slightly different results. The values listed for trace elements by different sources should, therefore, be regarded as indications of the order of magnitude of their abundances rather than precise determinations. The LREE and yttrium are most common and approximately as abundant in the crust as copper (Rudnick, 2005), whereas HREE, with the exception of yttrium, are significantly rarer (Figure 2). If one were to inspect a single atom in the Earth's upper continental crust at random, the chance of finding lutetium is less than 1 in 6 million. More specifically, REE occur practically everywhere in low concentrations, but only rarely assemble in quantities that are economically worth mining.

These elements are today essential in a wide range of high-tech processes and products. To name only a few, they are used in permanent magnets in wind turbines and in electric car engines, but also in catalytic converters for internal combustion engine vehicles and in petroleum refinery. They are used in the phosphors that make a smartphone screen shine bright, but also as polishing powder during thinning of its liquid crystal display to make the device thin and light. For over a century they have been used to create the sparks in gas lighters and in incandescent mantles for street gas lights, but they also produce powerful laser beams that cut and weld metal and perform a range of medical treatments. Commonly, the REE contribute a small amount of mass to an application, yet fulfil an essential function that is difficult to

substitute by other elements. In other words, REE have highly diverse applications and are intertwined with many aspects of our everyday life.

The reliable, affordable, and sustainable supply of raw materials is a topic of growing importance and concern in the European Union (EU) and elsewhere in the world. To begin to address these challenges, the European Commission (EC) launched its raw materials initiative in 2008 (European Commission, 2008). Subsequently, the EC evaluated non-energy mineral raw materials according to their economic importance and supply risk in the EU. Commodities that have both a large economic importance and a high risk of supply shortage are identified as critical raw materials (CRM) (European Commission, 2011). The purpose of the CRM list is to support the EU with a factual basis for policy-making, trade agreement negotiations, identifying investment needs and opportunities, and as a guide for research and innovation funding (European Commission, 2020a).

Rare-earth elements, as a single group, were identified in the first list along with 13 other CRMs (European Commission, 2011). In the first revision they were assessed separately as LREE, HREE, and scandium (European Commission, 2014). This division better reflects their distribution in different types of geological resources and where these are mined. Both LREE and HREE were regarded as critical in 2014 and scandium joined them in 2017 (European Commission, 2017, 2014). Gradually, the number of raw materials identified as critical has grown to 20 (European Commission, 2014) and after a revised methodology to 27 (European Commission, 2017). The fourth and latest list contains 30 CRMs (European Commission, 2020a).

In the context of CRMs, REE have received considerable attention. At the release of the first CRM list, the entire supply of REE was dependent on import from outside of the EU, mainly from China. In 2009, China produced 97 percent of the global REE supply and there were no viable alternatives for substitution by other elements or recycling from end-of-life products (European Commission, 2011). True to their name, the REE became short in supply when the Chinese government in September 2010 imposed an export ban to Japan for the purpose of geopolitical strong-arming (ERECON, 2015).

As a result of the tangible increase in supply risk, commodity prices soared. Economic speculation incentivised exploration companies (mainly juniors) to search for and evaluate hundreds of geological deposits of REE all around the globe, from the Arctic to the ocean floor. Many of the most successful projects focussed on REE-rich alkaline igneous rocks, including the Norra Kärr project (Bowell *et al.*, 2021; Saxon *et al.*, 2015). The endeavours of prospectors during the “REE Boom” have also contributed immensely to the scientific investigations into the characteristics of these REE mineralising systems, including this work.

Prices for REE reached their peak in Mid 2011, when a kilogram of europium oxide cost in excess of 4000 USD outside China. When the speculative bubble burst, prices quickly dropped and investments faded. Despite the intense exploration activity, the volatility of the stock market eventually left the EU not much closer to a reliable supply of REE than before the boom. In parallel with the preparation of the second list of CRMs, the EC therefore initiated a specific task group, the European Rare Earths Competency Network (ERECON), to evaluate and formulate policy options to secure the supply of REE for the EU over the course of one year (ERECON, 2015). The EC also supported the 2013–2017 EURARE project, which had a similar aim but a wider scope and included for example the development of ore-beneficiation schemes for partnered REE projects (EURARE, 2017; Goodenough *et al.*, 2016).

Despite all the efforts hitherto of working groups in various EU-funded projects consisting of academic, political, and industrial stakeholders, the EU is today not closer to practically realising a sustainable supply of REE than it was before 2010. Although the supply has diversified somewhat on the global scale, no new mines and production have opened in the EU and only a few percent of the demand could be satisfied by recycling of end-of-life products. The EU is completely reliant on import of both LREE and HREE: 99 and 98 percent, respectively, is supplied by China (European Commission, 2020a).

The supply of REE from China's quasi-monopoly is not only characterised by severe shortage risks due to geopolitical factors, but Chinese mining of REE has also been associated with significant environmental problems and illegal artisanal mining.

Chinese REE are primarily mined from three sources. The first is the Bayan Obo Fe–REE–Nb mine in Inner Mongolia, which is the largest known REE deposit in the world. The ore is enriched in LREE, which are mainly hosted in the minerals monazite and bastnäsite (Smith *et al.*, 2015). The tailings dams and environment near the Bayan Obo mine contain high concentrations of radioactive elements (Li *et al.*, 2016; Wang *et al.*, 2016) and have been portrayed by some journalists, who managed to get a close-up view (Maughan, 2015; Öhman, 2019).

The second deposit style is ion-adsorption clays (IAC), located in South China, which formed by weathering of granite. Rare-earth elements, predominantly HREE, are adsorbed onto clay minerals during the weathering process (Borst *et al.*, 2020; Xu *et al.*, 2017). They are easily extracted by mountain-top surface mining and heap leaching with sodium chloride or ammonium sulphate solution, even by artisanal miners. Toxic mining waste is disposed of in adjacent valleys and streams. Mining of IAC deposits was the main driver of land-use change in South China and until a few years ago contributed to approximately one third of China's total REE production (Yang *et al.*, 2013 and references therein). Since 2016, China has tightened its

environmental legislation to deal with the significant problems related to mining of IAC HREE deposits. As a result, domestic mining of Chinese IAC deposits has dropped off significantly. In 2020, China imported nearly half of its HREE feedstock, which was mined from IAC deposits in the neighbouring country of Myanmar, beyond the reach of Chinese environmental legislation. The 2021 coup d'état by the Myanmar military and COVID-19 have brought added instability to the supply of HREE to China, and therefore the global supply of HREE has been affected (Liang and Yin, 2021; Merriman and Embleton, 2021).

The third major Chinese REE resource is found in the Maoniuping mining area in the Sichuan Province. The Maoniuping ore is contained in LREE-enriched bastnäsite, which is hosted in nordmarkite stocks and carbonatite sills in a carbonatite-syenite complex (Xie *et al.*, 2009). High concentrations of contamination by toxic elements like Pb, Cd, and U have been determined in river sediments downstream from the REE mine (Wang *et al.*, 2018; Xu *et al.*, 2015).

The great tragedy of REE is thus that these elements, which are required to fulfil Europe's Green Deal, have largely been produced at the expense of the Chinese and Myanmar environment and public health.

The REE are therefore still identified as “bottlenecks” in particular for the sustainable production of permanent magnets used in wind turbines and electric motors. In the short term, the EU's demand for neodymium and praseodymium will likely double until 2030 and the demand for dysprosium may increase fivefold compared to today by an increased demand from renewable energy and e-mobility only (European Commission, 2020b).

A reliable and sustainable supply of REE is thus still far from being achieved, while the demand is projected to continue rising at an increasing rate. Since this fact poses a realistic challenge for the realisation of Europe's Green Deal, the EC continues to promote collective efforts, for example through the European Raw Materials Alliance (European Commission, 2020a; Gauß *et al.*, 2021), to reduce the EU's dependence on insecure supply chains of raw materials. Therefore, investigations into the origin and character of domestic geological deposits of REE, such as those hosted in alkaline igneous rocks, are in perpetuity of relevance in the larger scheme of providing the EU with long-term solutions for the sustainable supply of REE.

1.2 Rare rocks

Alkaline igneous rocks are the embodiments of a wide variety of magma compositions, processes, and origins, which are rare on a global scale. Daly (1914) estimated that the combined abundance of alkaline rocks constitutes less than one

percent of the total amount of subalkaline igneous rocks. Paradoxically, the rock names that geologists have invented to categorise the observed diversity within the alkaline rocks account for half of all names given to igneous rocks (Sørensen, 1974; definitions of common and uncommon mineral and rock names are compiled in Appendix II). While many of those names are obsolete or locally-named varieties of essentially similar rocks, it provides an illustration of both the intricacy and the vastness of the topic.

While their definition historically has been vague and inconsistent, it is today agreed upon that alkaline rocks are collectively characterised by their common denominators of being either silica-undersaturated or peralkaline or both (Sørensen, 1974). Carbonatites are igneous rocks that consist of a significant amount of carbonate minerals (Le Maitre, 2002), and thus are not alkaline rocks per the above definition. However, the minerals that coexist with the igneous carbonate minerals and the associated rocks, such as nepheline or melilitite, are normally alkaline or of an alkaline affinity, and carbonatites are therefore commonly also considered within the scheme of alkaline rocks (Mitchell, 2005).

Silica-undersaturated rocks contain a low abundance of Si relative to other major mineral-forming components like K, Na, Ca, Mg, and Fe. The total available Si is insufficient for all alkali elements to be incorporated into alkali feldspar and for all Mg and Fe to form orthopyroxene. Instead of feldspar and orthopyroxene, silica-deficient feldspathoid minerals and olivine may form, which are chemically unstable in the presence of quartz.

A rock's state of silica saturation can be inferred from observations made from its actual mineral composition (mode), where for example the presence of feldspathoids or olivine in the absence of orthopyroxene provide expressions of silica undersaturation. In rocks for which the mode cannot be determined, for example volcanic rocks that are too fine-grained or contain glass, silica saturation can be assessed by calculation of a standard mineral composition (CIPW norm) from a representative bulk chemical composition (Cross *et al.*, 1902). The normative mineralogy and calculated silica saturation result from a hierarchical allotment scheme for the major elements to Si to approximate observed mineral assemblages in natural rocks.

Peralkaline rocks contain a molecular excess of alkali elements over Al. In other words, they are alumina-undersaturated. Many of the commonest alkali-rich minerals, such as alkali feldspar and biotite, contain equal molecular amounts of Al and alkali elements, but this is also true for rare feldspathoid minerals like leucite and nepheline. The excess alkali in peralkaline rocks, which cannot be bonded to Al,

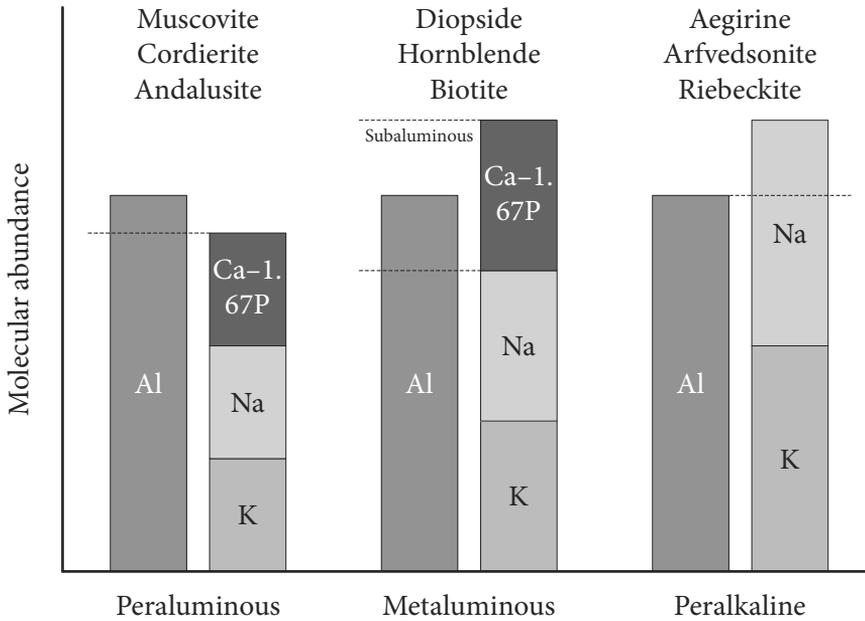


Figure 3. An illustration of the relative molecular abundances of Al, Ca, Na, and K in peraluminous, metaluminous, subaluminous, and peralkaline rocks, which are frequently reflected by the occurrence of characteristic minerals.

instead forms alkali-rich minerals without Al, such as aegirine, arfvedsonite, and riebeckite (Figure 3), or more exotic minerals like ussingite and zirsinalite.

Contrary to silica saturation, which requires the calculation of a norm, a meaningful aluminium saturation index (ASI) and alkalinity index (AI) can simply be calculated from the molecular proportions of Al, Ca (corrected for Ca allotted to P in apatite), and alkalis. The ASI is defined as $ASI = Al / (Ca - 1.67P + Na + K)$ and AI is defined as $AI = Al - (Na + K)$ (Frost and Frost, 2008; Shand, 1947; Zen, 1988). Rocks with $ASI > 1$ are peraluminous whereas those with $ASI < 1$ are subaluminous. Subaluminous rocks with $AI > 0$ are metaluminous whereas those with $AI < 0$ are peralkaline (Figure 3). Commonly, the Agpaite Index (sometimes also called Alkalinity Index or Peralkalinity Index) is also used (Ussing, 1912), which is defined as the molecular ratio of alkalis to Al ($[Na + K] / Al$) and for peralkaline rocks is larger than 1.

The meaningfulness of these indices is inferred from the observation that in nature the alkali elements have a preferential affinity to Al, hosted in feldspar and feldspathoids, more so than other elements. Therefore, K and Na are also the first elements to be allotted to Al in normative calculations from a bulk chemical composition. Peralkalinity results in the presence of *acmite* (aegirine) and sodium metasilicate (Na_2SiO_3) components in the calculated norm (Cross *et al.*, 1902).

These two characteristics of alkaline igneous rocks—silica undersaturation or peralkalinity or both—result in a broad grouping into three categories:

1. Metaluminous (or rarely peraluminous) and silica-undersaturated,
For example: diopside nephelinite,
2. Peralkaline and silica-(over)saturated,
For example: riebeckite granite,
3. Peralkaline and silica-undersaturated,
For example: aegirine nepheline syenite.

The broad definition of alkaline igneous rocks results in a diverse clan, whose differences in terms of origin, mineral and chemical composition, and mode of occurrence may be larger than their common characteristics. Not all alkaline rocks have a common origin (Sørensen, 1974). This thesis will primarily investigate alkaline rocks that belong to the third category, with a more indepth discussion about their origin in Chapter 4.

1.2.1 Agpaitic rocks

Agpaitic rocks are highly peralkaline igneous rocks that are defined by the occurrence of complex silicate minerals that are rich in high-field-strength elements (HFSE: Zr, Ti, Nb, REE, etc.) and fluorine and other volatile elements, such as eudialyte and rinkite. These complex minerals occur instead of simple minerals like zircon and titanite, which occur in miaskitic rather than agpaitic rocks (Sørensen, 1997, 1960). The type locality for agpaitic rocks is the Ilímaussaq alkaline complex in South Greenland, where the term “agpaite” was introduced by Ussing (1912) for nepheline syenites with a molecular ratio of $(\text{Na}+\text{K})/\text{Al} \geq 1.2$ to distinguish the rocks of Ilímaussaq from ordinary nepheline syenites without these complex HFSE minerals. However, this geochemical discrimination is unsatisfactory for its intended purpose, since not all rocks carrying characteristic agpaitic minerals comply with this rule. A descriptive mineralogical definition is therefore still maintained to define agpaitic rocks irrespective of their bulk composition (Marks and Markl, 2017).

The eudialyte-group minerals (EGM) are the hallmark of agpaitic rocks, often occurring as eye-catching deep red crystals. The name derives from the Greek language and means “easily dissolved”, denoting its property of readily decomposing in weak acid (Stromeyer, 1819). The first specimens of eudialyte were collected from the Ilímaussaq alkaline complex by Karl Ludwig Giesecke in 1806 (Giesecke, 1878; Sjöqvist, 2019; Stromeyer, 1819). They are highly complex trigonal cyclosilicate minerals, which comprise both three-fold $(\text{Si}_3\text{O}_9)^{6-}$ and nine-fold $(\text{Si}_9\text{O}_{27})^{18-}$ rings,

and can incorporate varying amounts of Na, Ca, Fe, Mn, REE, Sr, Zr, Nb, K, Ti, H, and W (Johnsen *et al.*, 2003; Rastsvetaeva and Chukanov, 2012).

The generalised chemical formula for EGM, which in some cases may be unsatisfactory (Rastsvetaeva, 2007), is $[N(1)N(2)N(3)N(4)N(5)]_3[M(1.1)M(1.2)]_3[M(2.1)M(2.2)M(2.3)]_{3-6}[M(3)M(4)]Z_3[Si_{24}O_{72}]\Theta_4X(1)X(2)$, where each crystal site (N , M , Z , Θ , and X) can be occupied by the following elements, not including minor substitutions (Johnsen *et al.*, 2003):

$N(1-5)$: Na, H_3O^+ , K, Sr, REE, Ba, Mn, or Ca;

$M(1)$: Ca, Mn, REE, Na, Sr, or Fe;

$M(2)$: Fe, Mn, Na, Zr, Ta, Ti, K, Ba, or H_3O^+ ;

$M(3)$ and $M(4)$: Si, S, Nb, Ti, W, or Na;

Z : Zr, Ti, or Nb;

Θ : O, OH, or H_2O ;

$X(1)$ and $X(2)$: Cl, F, H_2O , OH, CO_3 , SO_4 , AlO_4 , or MnO_4 .

Given the range of possible site occupations, substitutions, and vacancies in combination with the tendency for elements (*e.g.* Mn) to be able to occupy multiple crystal sites, it is virtually impossible to calculate wholly reliable crystal chemistry and end-member compositions from a chemical analysis only. The only practical mineral-chemical “constant” in use is often given as $Si + Al + Zr + Ti + Hf + Nb + Ta + W = 29$ *apfu* (atoms per formula unit) (Johnsen and Grice, 1999). However, most EGM from the Lovozero alkaline massif, one of the largest occurrences of EGM in the world, have a Zr content in excess of 3 *apfu*, thus calling into question the generalised use of the 29 *apfu* rule or at least rendering it inappropriate for hyperzirconian EGM (Mikhailova *et al.*, 2020; Panikorovskii *et al.*, 2021). A simplified cation site assignment based on the results of a chemical analysis is commonly applied (Pfaff *et al.*, 2010), although a reliable cation assignment and end-member determination without the use of single-crystal X-ray diffraction is unlikely.

If alkaline igneous rocks are rare among igneous rocks, then agpaitic rocks are rare even among alkaline igneous rocks. Just over 100 occurrences of rocks containing EGM are known (Marks and Markl, 2017). Paradoxically, some of these are relatively large magmatic intrusions, including Khibina (9100 km³) and Lovozero (1600 km³)

in Kola Peninsula (Arzamastsev and Mitrofanov, 2009) and Ilímaussaq (200 km³) in South Greenland (Larsen and Sørensen, 1987).

Agpaitic rocks are famed for their mineral wealth, both in terms of the exoticness and the diversity of different minerals that can be found in one locality. Some agpaitic minerals are relatively common but extremely complex (*e.g.* eudialyte) (Johnsen *et al.*, 2003; Rastsvetaeva, 2007; Rastsvetaeva and Chukanov, 2012), while others are relatively simple but occur as major cumulus phase in one place in the world (*e.g.* naujakasite) (Khomyakov *et al.*, 2001). Approximately 80 water-soluble minerals, some of which form part of the magmatic mineral assemblage (*e.g.* villiaumite), have been found in the most evolved varieties of agpaitic rocks and associated hydrothermal alteration (Khomyakov, 1995). Some occurrences are among the most mineral diverse in the world. Khibina contains 531 different minerals, 122 of which have their type locality (TL) there (Mindat, 2021a). Other well-known mineral localities include Mont Saint-Hilaire 433 (71 TL), Lovozero 397 (109 TL), and Ilímaussaq 234 (38 TL) (Mindat, 2021b, 2021c, 2021d).

1.3 Rare elements in rare rocks

Alongside their exotic minerals, agpaitic rocks are also characterised by extreme chemical bulk compositions. They tend to be rich in elements such as Na, Li, Be, Zr, Nb, Zn, Sn, Rb, Ga, REE, F, and Cl, whereas their content of Mg, Ni, Cr, Co, and Sc and in many cases Ca, Sr, and Eu is depleted (Bailey *et al.*, 2001; Sørensen, 1997). It has been recognised for a long time that agpaitic nepheline syenites, due to their unusual mineralogy and geochemistry, could form potential polymetallic ore deposits of rare elements, with emphasis on elements that are of increasing importance in high-technology applications (Semenov, 1974; Sørensen, 1992).

Rare-earth elements are generally enriched in agpaitic rocks, which are the host rocks of important REE mineral deposits globally and in Europe (Goodenough *et al.*, 2016; Smith *et al.*, 2016). The deposits are commonly orthomagmatic or contact metasomatic (fenite), which means that the whole rock mass can often be regarded as a mineral deposit. Mineral deposit grades are typically in the order of 0.1–1.0 wt.% total rare-earth oxide (TREO) and can be hosted among others in one or more minerals of the eudialyte, steenstrupine, perovskite, rinkite, and britholite groups (Dostal, 2017; Sørensen, 1992).

“

Men will be taught that beneath and behind all the outward beauty of our lowlands, our uplands, and our highlands there lies an inner history which, when revealed, will give beauty a fuller significance and an added charm.”

—Sir Archibald Geikie (1905)

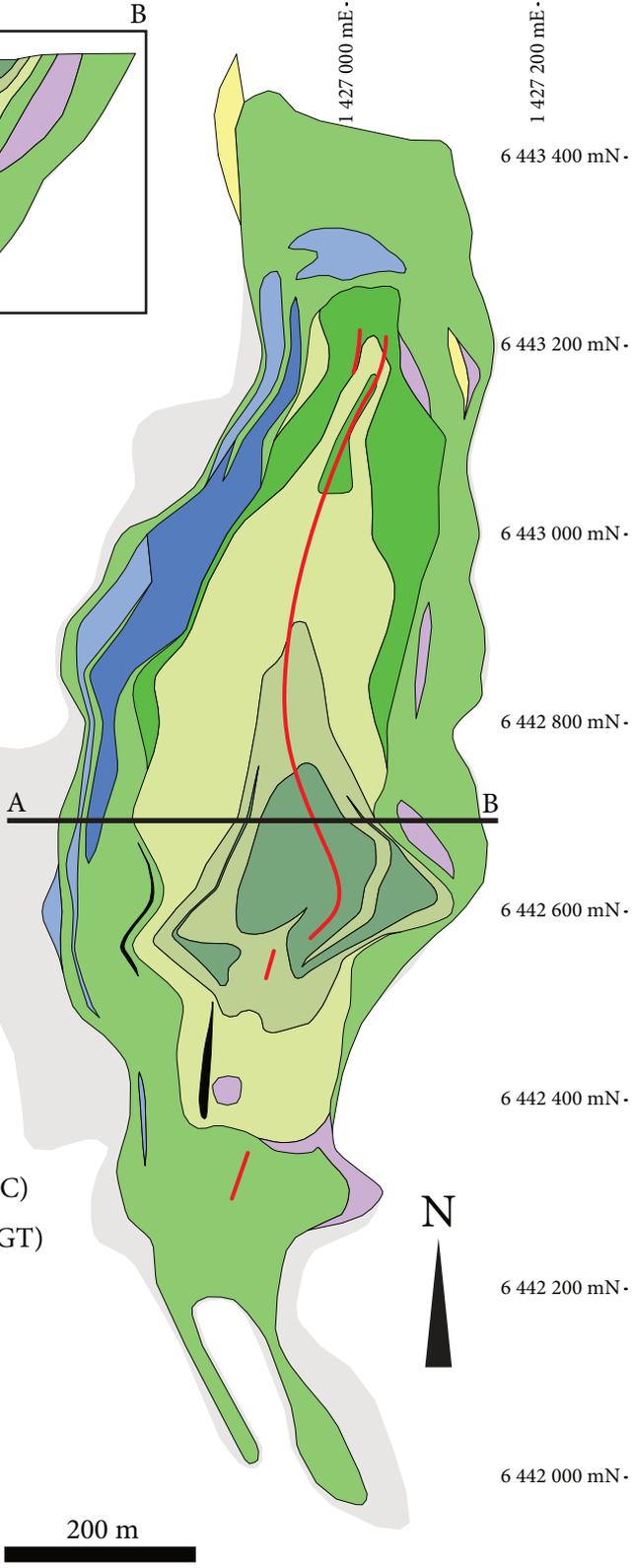
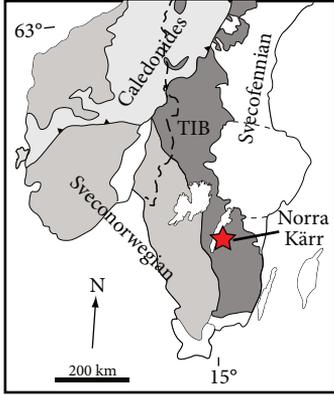
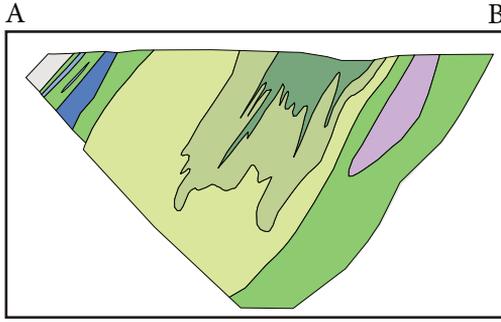
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Norra Kärr Alkaline Complex

THE NORRA KÄRR alkaline complex is a classic locality of agpaitic alkaline rocks, located in southern Sweden close to the eastern shore of Lake Vättern (58°06'N, 14°34'E; Figure 4). It has been investigated by geologists for 120 years, but has received an upswing in national and international attention during the last decade since it was revealed as a unique deposit of heavy rare-earth elements, zirconium, and niobium hosted in nepheline syenite.

2.1 Research history

A small body of alkaline rocks was discovered by K.E. Norman at Norra Kärr farm on the border between Jönköping and Östergötland County during regional geological mapping at the turn of the previous century for the map sheet “Gällö” by the Geological Survey of Sweden (Blomberg, 1906). At this time, only two other localities of alkaline rocks were known in Sweden: Alnö and Särna. The newly discovered exotic rocks attracted the attention of Alfred Elis Törnebohm. In the Summer of 1905, he conducted a detailed study of the area together with Axel Hamberg. Törnebohm presented the results, illustrated by numerous maps and rock samples, at a meeting of the Swedish Geological Society on 7 December 1905 (Munthe, 1905).



Legend

-  TIB granitoids
-  Fenite aureole
-  Pulaskite (PUL)
-  - with grennaite
-  Lakarpite
-  Kaxtorpite (KAX)
-  Grennaite (GT)
-  - with catapleiite (GTC)
-  - with pegmatoids (PGT)
-  - migmatized (GTM)
-  Alkaline unspecified
-  Mafic rocks
-  Mafic dyke

Geology at 200 m above sea level

Projection: RT90 2.5 gon väst

Törnebohm's petrographic investigation of the fine-grained green rocks demonstrated the presence of eudialyte as a common constituent in addition to the more customary minerals nepheline, feldspar, and aegirine. He also described the abundant presence of catapleiite, which was not known as a dominant rock-forming mineral from any other locality. For that reason, the rock was named "catapleiite syenite". A variety of amphibole-bearing syenite was also discovered, occurring as enclosed rock units, which were named "lakarpite" after the nearby farm Lakarp (Blomberg, 1906; Törnebohm, 1906).

Norra Kärr was afterwards only sparsely mentioned in the literature (Backlund, 1932; Gavelin, 1912; Geijer, 1922) until a detailed follow-up to Törnebohm's pioneering work commenced in the early 1940s by Olge Jungstedt Adamson under the supervision of Percy Quensel. Adamson's doctoral dissertation was held on 13 May 1944 in Stockholm (Adamson, 1944). His work resulted in a more detailed geological map and thorough petrographic descriptions of the alkaline rocks. Adamson renamed Törnebohm's catapleiite syenite and called it "grennaite" after the nearby town of Gränna, which is the local rock name it has been known by since then.

Harry von Eckermann and Hans Koark worked in parallel in the late 1950s and during the 1960s. They released their first results in time for the excursion to Norra Kärr organised in conjunction with the 21st International Geological Congress (Koark, 1960; Von Eckermann, 1960). They held different views on the genesis of Norra Kärr. Von Eckermann argued for a wholly igneous development whereas Koark invoked deformation and metamorphic overprinting to explain certain structural aspects (Koark, 1969, 1960; Von Eckermann, 1968, 1960).

Between the 1960s and the conception of the work presented here, only spurious scientific articles and notes have been published, mainly concerning aspects of isotope geochemistry (Bibikova *et al.*, 1980; Blaxland, 1977; Kramm and Koark, 1988; Patchett *et al.*, 1981) and mineralogy (Holtstam, 1998; Oberti *et al.*, 2009).

The mineral exploration rights encompassing the Norra Kärr alkaline complex were claimed by Tasman Metals Ltd. (currently Leading Edge Materials Corp.) in 2009, before the REE boom of 2010. Through the company's efforts, Norra Kärr developed from a promising REE prospect to one of the largest defined REE resources in mainland Europe, signified by a rare high abundance of the heavy rare-earth elements (Nebocat, 2009; Reed, 2011; Davidsson *et al.*, 2015; Howell *et al.*, 2021). As a result,



Figure 4. Geological map of the Norra Kärr alkaline complex at 200 m above sea level and as a vertical section at line AB. The location of Norra Kärr in relation to regional geological provinces is shown on the inset map. Map modified from Saxon *et al.* (2015) and Sjöqvist *et al.* (2020).

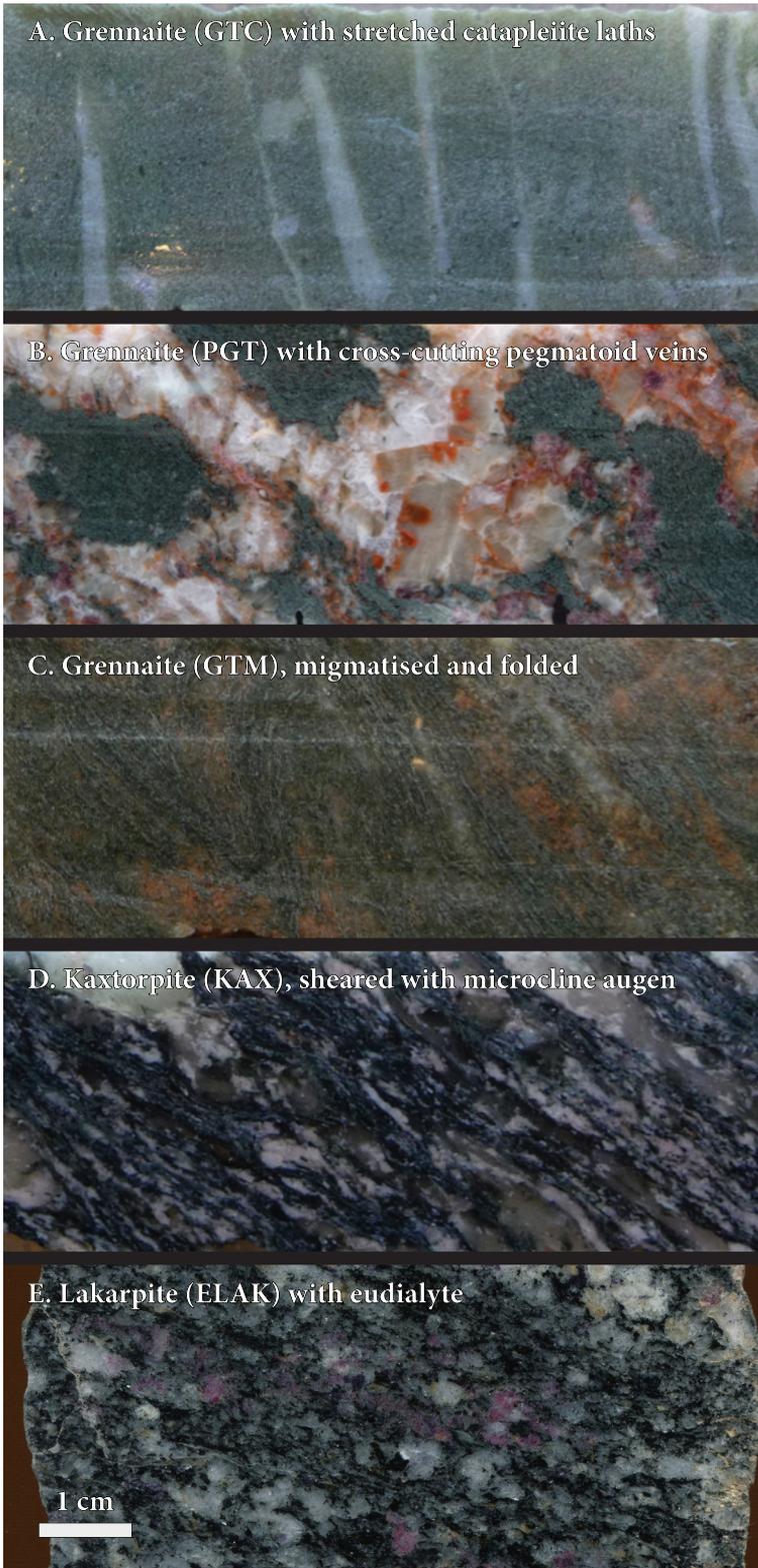


Figure 5. The major rock types of the Norra Kärr alkaline complex. A. Grennaite (GTC) with large stretched catapleiite laths and streaks. B. Grennaite (PGT) with coarse-grained leucocratic pegmatoid veins, rich in eudialyte and catapleiite, in a fine-grained grennaite host rock. C. Grennaite (GTM) from the centre of the complex with a migmatized and folded texture. D. Kaxtorpite (KAX), sheared with large microcline augen. E. Lakarpite (ELAK) with eudialyte and mosandrite-(Ce). Sample from the “Discovery Outcrop”. A–D are photographs of cut drill core, E is a photograph of a polished rock slab. Modified from Sjöqvist *et al.* (2013).

Norra Kärr has been identified as a mineral resource of national interest and international importance (Eilu *et al.*, 2021; Goodenough *et al.*, 2016; SGU, 2011).

The last decade has therefore seen an influx in research activity surrounding Norra Kärr as an interesting mineral deposit, resulting in academic papers on a wide array of topics such as a life cycle assessment of dysprosium production from eudialyte, laser-based spectroscopic method development, and an investigation into the biogeochemical signature of the agpaitic rocks (Bluemel *et al.*, 2013; Romppanen *et al.*, 2019; Zapp *et al.*, 2018).

Simultaneously and in parallel with my own work, Petya Atanasova has completed a doctoral dissertation on other geological aspects of Norra Kärr (Atanasova, 2020). Both of our academic endeavours have benefitted from the generous access to samples and data as well as support by staff of the exploration company.

2.2 Geology and mineralogy

The Norra Kärr alkaline complex is a relatively small intrusion that consists of varieties of peralkaline nepheline syenite with characteristic agpaitic minerals. It is approximately 1400 m by 450 m oriented north-south with its long axis (Figure 4). The outline of Norra Kärr marks a depression in the surrounding landscape. The bedrock is covered by a thin layer of glacial till, peat bogs, coniferous forest, dense spruce plantations, and overgrown pastures belonging to the relinquished Norra Kärr farm. Moss and lichen seem to thrive on the feldspar- and nepheline-rich outcrops. As a result, the bedrock exposure is, on the whole, relatively sparse, which has hampered historical investigations and modern excursions.

The bedrock surrounding the Norra Kärr alkaline complex is regionally dominated by granitoids belonging to the 1.81–1.76 Ga Småland-Värmland Belt of the 1.85–1.65 Ga Transscandinavian Igneous Belt (TIB), which is a north-south trending array of batholiths that formed in a continental-arc tectonic setting and occurs from Lofoten to Blekinge (Högdahl *et al.*, 2004; Sjöqvist *et al.*, 2017). To the west of Lake Vättern the bedrock is overprinted by both 1.4 Ga Hallandian and 1.1–0.9 Ga Sveconorwegian high-grade orogenic metamorphism (*e.g.* Andersson, 2001; Austin Hegardt, 2010; Brander, 2011). The Sveconorwegian Frontal Deformation Zone (SFDZ), a north-south trending zone of anastomosing shear zones, coincides approximately with Lake Vättern and delineates the eastern extent of Sveconorwegian metamorphism (Wahlgren *et al.*, 1994). The western structural hanging wall to Norra Kärr contains ultramylonite shear zones that belong to the SFDZ (Ranjer, 2013; Sjöqvist *et al.*, 2014).

In addition to the SFDZ, the term Protogine Zone (PZ) has also been used to describe the north-south trending boundary between gneisses in the west and undeformed



Figure 6. Grennaite (PGT) consisting of a fine-grained groundmass with thin leucocratic apgaitic veins and a cross-cutting coarse-grained apgaitic pegmatoid. Photograph of a polished rock slab.

granites in the east, approximately centred on the location of Lake Vättern. The PZ has been interpreted as an older, pre-Sveconorwegian zone of weakness in the Baltic Shield, which has seen repeated pulses of magmatic activity at least at 1.56, 1.46–1.44,

1.22, and 1.20 Ga (Brander and Söderlund, 2009; Claeson and Persson, 2019; Larsson and Söderlund, 2005; Söderlund and Ask, 2006), including the Jönköping anorthositic suite (1.46 Ga), Vaggeryd syenite pluton (1.22 Ga), Smålands Taberg ultramafic intrusion (1.20 Ga), and an undated augite syenite at Virestadsjön. The location of Lake Vättern also marks the position of a Neoproterozoic rift basin that is filled with syntectonic sediments belonging to the Visingsö group of Tonian age (Moczyłowska *et al.*, 2018), which, together with Cambro-Silurian sedimentary cover rocks beneath the Östgöta plains further north, represent the youngest rocks in the vicinity of Norra Kärr.

The Norra Kärr alkaline complex intruded the TIB at 1.49 ± 0.01 Ga (2σ), determined by U–Pb dating of metasomatic zircon that formed during alkaline contact alteration (Sjöqvist *et al.*, 2017). The dominant rock type in Norra Kärr consists of several varieties of the locally-named “grennaite”, constituting approximately 80 % of the known volume (Saxon *et al.*, 2015). Grennaite is a fine-grained, nearly aphanitic, green agpaitic peralkaline nepheline syenite that chiefly consists of nepheline, albite, microcline, aegirine, and eudialyte regularly with catapleiite (Adamson, 1944; Törnebohm, 1906). Grennaite shows both mineralogical and geochemical similarities to lujavrite and has been called “micro-leucolujavrite” (Sørensen, 1974, p. 565). It occurs in several varieties. The most characteristic is the catapleiite-porphyrritic grennaite (GTC; Norra Kärr rock codes are summarised in Appendix III), which contains fine-grained eudialyte in its groundmass and coarse-grained bluish-grey catapleiite laths or impure rounded and stretched catapleiite-rich “streaks”, which can be several centimetres long (Figure 5A). A eudialyte-porphyrritic grennaite variety (GTCE) is also found, although it is not abundant. Here, catapleiite commonly forms rims on the centimetre-sized round eudialyte grains, as well as rims of rinkite-group minerals (Atanasova *et al.*, 2017). The porphyritic grennaite varieties are grouped into a “GTC” domain.

Another variety of grennaite, without porphyritic catapleiite and eudialyte, is characterised by an abundance of medium- to coarse-grained leucocratic pegmatoid (= nepheline syenite pegmatite) veins and dykes in a fine-grained green grennaite groundmass (Figure 5B) and is thus named the “PGT” domain. It is subdomained according to the relative amounts of pegmatoid veins and fine-grained groundmass (GT1, GT2, GT3, GTP, PGT, NEP, and GTR). The pegmatoid veins are generally composed of the same minerals as the groundmass grennaite, although albite is a subordinate mineral. They are rich in nepheline and microcline, with abundant eudialyte and sometimes euhedral catapleiite laths. Aegirine is the dominant mafic mineral in the pegmatoids, and alkali amphiboles are rare. The pegmatoids vary in size from veins less than a centimetre wide to dykes that have been intersected in drill core for several metres. Small veins tend to be parallel to the schistosity of the host grennaite, whereas larger veins and dykes cross-cut the foliation (Figure 6). The

schistosity commonly sweeps around larger pegmatoidal pods. With the exception of a medium-grained foliated and recrystallised pegmatoid variety (GTR), the pegmatoids are internally undeformed.

The third major variety of grennaite is recognised near the centre of the intrusion, the so-called “GTM” domain. It is characterised by a lighter colour and recrystallised texture that resembles a migmatite (Figure 5C). Pegmatoids are rare in the GTM domain. This grennaite variety has a somewhat mottled appearance and is rich in orange-red natrolite-subgroup minerals and orange-brown EGM.

The grennaite encloses a number of bodies of other alkaline rocks, which all have in common that they are phanero-crystalline rocks, in contrast with the fine-grained grennaite. Adamson (1944) divided the enclosed rocks into two categories: 1) lakarpite and pulaskite group, with Zr hosted in rinkite-group minerals, and 2) “kaxtorpите” group, which does not contain zirconsilicate minerals. Kaxtorpите is named after the nearby farm Kaxtorp.

Kaxtorpите is centrally located and enveloped by the GTM domain. It is a foliated to schistose nepheline syenite containing fluoro-leakeite and aegirine, commonly with coarse-grained microcline porphyroblasts (Figure 5D). It contains variable amounts of (decomposed) nepheline, albite, pectolite, and titanite (Adamson, 1944), as well as minor lorenzenite and willemite.

In addition to the centrally located kaxtorpите, the grennaite contains numerous bodies of enclosed alkali (nepheline) syenites and poorly characterised alkaline mafic rocks, occurring from cobble-sized enclaves to larger continuous bodies over one hundred metres long. These are mainly pulaskite and lakarpite.

The rock referred to as pulaskite is a medium-grained alkali syenite that mainly consists of microcline and albite feldspar with varying amounts of alkali amphibole, aegirine, and phlogopite, as well as spurious nepheline (Adamson, 1944). Lakarpite is an alkali nepheline syenite that is rich in alkali amphibole and albite. The distinction between pulaskite and lakarpite is probably not entirely consistent and they are texturally similar. Adamson used the term pulaskite to describe a slightly silica-undersaturated microcline-rich rock with arfvedsonite, aegirine, biotite, and minor nepheline. Lakarpite, on the other hand, defined a nepheline-rich variety with minor microcline (Adamson, 1944). Pulaskite and lakarpite are serially related rock types. Both are transitional between miaskitic and agpaitic syenite and contain both rinkite-group minerals (Sokolova and Cámara, 2017) as well as titanite (Adamson, 1944) and zircon in direct association with the rinkite group (Andreas Karlsson, pers. comm). Both pulaskite and lakarpite commonly contain abundant purple fluorite. An agpaitic variety of lakarpite (ELAK), found mainly in the eastern part of Norra Kärr, is rich in



Figure 7. Isoclinal folding observed in a kaxtorpite outcrop.

eudialyte and mosandrite-(Ce) especially at the so-called “Discovery Outcrop” (Figure 5E) (Sjöqvist *et al.*, 2013), although observations from drill cores indicate that its eudialyte content is spatially linked to the contacts with the agpaitic grennaite that encloses it. Lakarpite and pulaskite occur both as massive and gneissic varieties.

Surrounding the Norra Kärr alkaline complex, the TIB granitoids have been affected by syn-magmatic alkaline metasomatic alteration (fenitisation), which has transformed the country rocks into a fenite aureole composed of a biotite- and aegirine-augite-bearing syenitic rock (Adamson, 1944; Christensson, 2013; Sjöqvist *et al.*, 2017). At the surface level, fenitisation is most pronounced in the western hanging wall, extending out more than 100 m, whereas it is almost absent in the eastern granite (Adamson, 1944). However, in drill core it can be observed that fenitisation in the eastern contact is more pronounced at depth (Sjöqvist *et al.*, 2017).

The lithological domains of Norra Kärr occur in a concentric arrangement, both in plan view and in a vertical section (Figure 4). GTC with enclosed PUL and LAK occurs at the margins, followed by GT, PGT, and GTM, which envelopes a central enclosed unit of KAX. All rock types are characterised, at least locally, by a pronounced foliation or schistosity with a north-south strike, dominantly dipping steeply to the west. Adamson found the schistosity to conform exactly to the outer margin of the intrusion, which as far as he knew was roughly oval shaped (Adamson, 1944), but results from drilling have drastically modified the identified shape of the

intrusion. Von Eckermann dug up the contact to the foliated granite at the northern contact and found the schistosity to run parallel to the east-west striking contact to the fenitized granite (Von Eckermann, 1968). Although Adamson (1944) documented the occurrence of schistosity and cataclastic deformation within KAX, he failed to discuss the intense isoclinal folding in the centre of the intrusion, which can be observed in KAX and in GTM (Figure 5D & 7). Other effects of metamorphic overprinting can be detected for example by the jadeite-rich composition of clinopyroxene in grennaite (Atanasova *et al.*, 2017) and the Sveconorwegian age of pegmatoid veins in the PGT domain, indicating they formed by low-temperature partial melting of grennaite (Sjöqvist *et al.*, 2020).

It has been suggested that the concentrically-arranged units originally formed in a layered lopolithic intrusion, with GTC at the bottom and KAX at the top, which subsequently was compressed and stretched during Sveconorwegian metamorphic overprinting and deformation into its current elongated bowl shape (Atanasova *et al.*, 2017; Saxon *et al.*, 2015). If this hypothesis were correct, the roof of the Norra Kärr intrusion is no longer present and the remaining body represents only the lower portion of the original lopolith. The axial plane of the Norra Kärr syncline is intruded by a north-south trending mafic dyke (Saxon *et al.*, 2015) of unknown age, which cuts across the foliation in the alkaline rocks.

Adamson lamented, “There is unfortunately only a small difference in level within the Norra Kärr district, so the geological structure of the rock mass cannot be submitted to a closer study, which would probably have contributed to the solution of the problem of the textural development of grennaite” (Adamson, 1944, p. 238). In other words, new data from rock drill cores have completely altered the geological understanding of the lithology and structure, and have overthrown Adamson’s idea of an oval-shaped stock with perfectly conformable “precrySTALLINE character of the schistosity” in grennaite (Adamson, 1944, p. 236).

2.2.1 Eckermannite and fluoro-leakeite

It is worth mentioning explicitly that, during his comprehensive petrographical work, Adamson discovered and described a new alkali amphibole in kaxtorpites from Norra Kärr, which he named eckermannite after Swedish geologist Harry von Eckermann (Adamson, 1942). The chemical analysis of the amphibole, however, turned out to be incomplete and was missing a significant amount of lithium (Sundius, 1945). Much later, another alkali amphibole was described from the same locality, named fluoro-aluminoleakeite (Oberti *et al.*, 2009). These two minerals turned out to be one and the same and therefore it was decided to move the type locality for the original eckermannite to Myanmar, while Adamson’s amphibole is now known as fluoro-leakeite and has its type locality in Norra Kärr (Hawthorne *et al.*, 2012; Oberti *et al.*,

2015). Li₂O contents of up to 1.7 wt.% were measured in fluoro-leakeite from kaxtorpite by LA-ICP-MS (Eriksson, 2016).

2.3 Geochemistry: major, minor, and trace elements

The unpublished geochemical data discussed here are derived from a summarised version of the extensive database of analyses, which in total contains 9986 bulk rock analyses, supplied by Leading Edge Materials Corp. The entire drilled intersection through the body of alkaline rocks was routinely sampled with a standard 2-metre sample length and assayed by lithium-metaborate fusion ICP-MS and XRF by ALS Chemex in Vancouver, Canada (method ME-MS81 complemented by ME-XRF10 for Zr grades >10000 ppm). The company employed a rigorous QA/QC programme to verify and validate the geochemical data (Bowell *et al.*, 2021).

The alkaline rocks at Norra Kärr have an extreme and anomalous geochemical composition compared to most other rocks found in the Earth's crust. The rocks are mildly to highly peralkaline and dominantly silica undersaturated. Some elements that are normally major elements occur here as trace elements (*e.g.* Mg), and vice versa (*e.g.* Zr).

The CIPW norm was defined before the classification of agpaitic rocks and does not take into account the exotic agpaitic minerals and geochemistry and should therefore be used indicatively. For example, the significant content of Zr, which is hosted in silicate minerals with a lower Zr content than the zircon component in the norm, contributes to the undersaturation of silica, unaccounted for by the CIPW norm. Nonetheless, all rock compositions in Norra Kärr result in a calculated acmite component and the most peralkaline varieties also invoke the sodium metasilicate component. According to the norm, pulaskite and lakarpite are more or less saturated in silica, whereas kaxtorpite and grennaite are strongly undersaturated in silica. This is largely consistent with their mineral modes and the observed absence of quartz-bearing rocks in Norra Kärr.

All lithological units in Norra Kärr are subaluminous ($0.62 < \text{ASI} < 0.86$) and mildly to strongly peralkaline despite being relatively rich in Al₂O₃; ranging from 13.6 wt.% in kaxtorpite to 19.4 wt.% in catapleiite- and eudialyte-bearing grennaite (GTCE subdomain). The alkalinity index (agpaitic index in parentheses) varies from approximately -0.02 (AI: 1.1) in pulaskite and lakarpite, to -0.08 (AI: 1.2) in kaxtorpite, -0.09 (AI: 1.2) in the GTC and GTM domains in grennaite, and -0.1 (AI: 1.3) in PGT grennaite. The kaxtorpite and the PGT grennaite domains are even persodic (molecular Na > Al). Nepheline syenites in Norra Kärr have extreme (molecular) Na/K ratios, ranging from 2.1 in pulaskite and lakarpite to on average 4.7

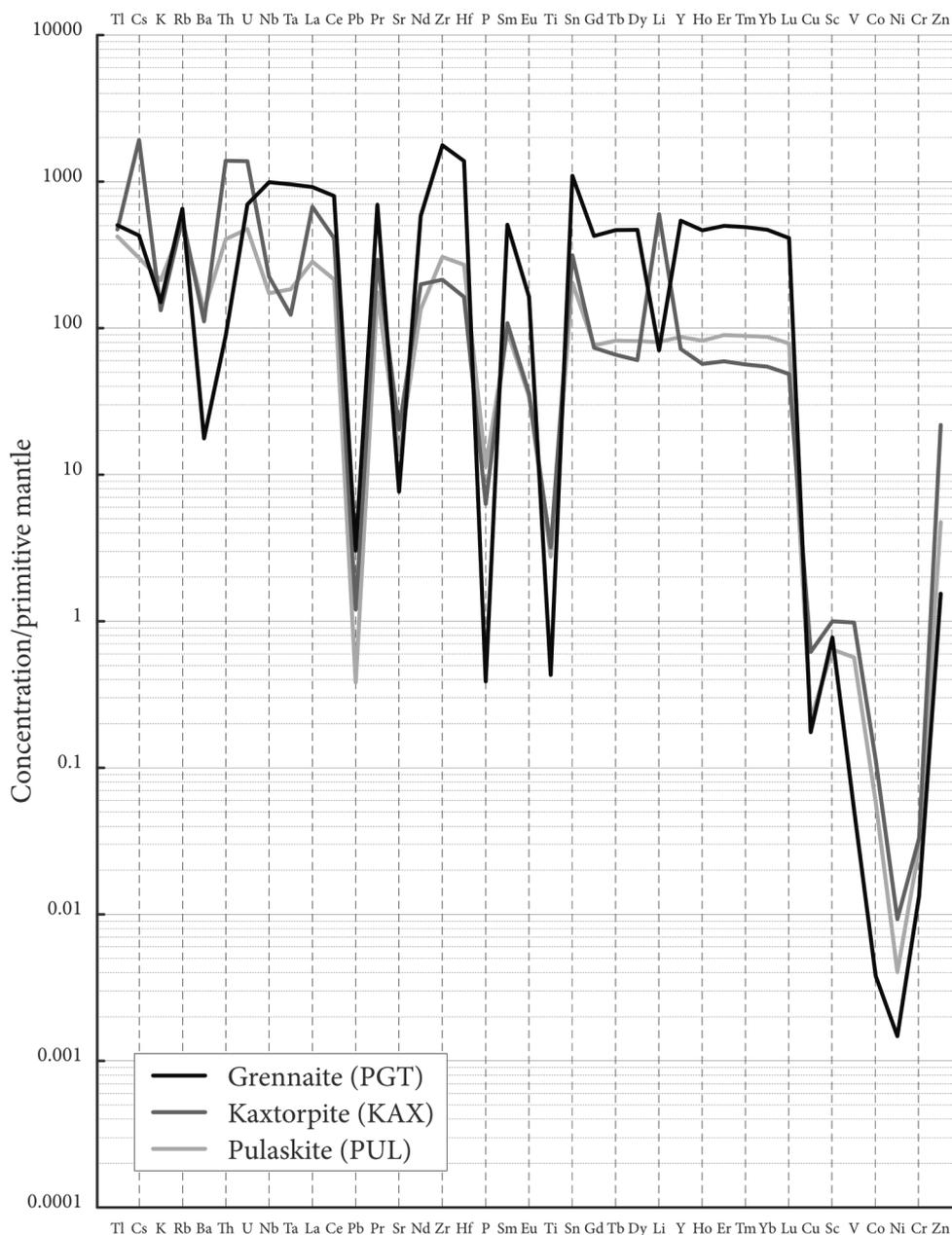


Figure 8. Trace element profiles for pulaskite (PUL), kaxtorpite (KAX), and grennaite with pegmatoids (PGT), normalised against primitive mantle (Lyubetskaya and Korenaga, 2007)

in PGT but reaching up to 5.9 in the GT2 subdomain, compared with 4.56 in the hyperagpaitic naujakasite lujavrite of Ilímaussaq (Khomyakov *et al.*, 2001).

The most incompatible elements (Zr, Hf, Sn, Ta, REE, Nb, Rb, Cs, Se, Sn, Tl) are relatively consistently enriched to concentrations that are approximately three orders of magnitude higher in grennaite than the primitive mantle (Lyubetskaya and Korenaga, 2007), reaching the highest degree of enrichment in the PGT grennaite domain (Figure 8), which contains on average 2.01 wt.% ZrO₂. The large-ion lithophile elements (LILE) Na, Cs, and Rb are highly enriched, while the content of K, Sr, Pb, Ba, and Eu is depleted relative to the other LILE. Other incompatible elements (As, Be, Bi, Cd, Li, Mo, Re, Te, Th, etc.) are elevated to lower degrees of enrichment and indicate variable trends, possibly witnessing that they may have behaved both as compatible and incompatible during different stages of magma differentiation.

The most compatible elements, which are depleted relative to primitive mantle, are Ni, Co, Mg, Cr, V, Fe, Cu, S, P, Ti, Ca, In, and Sc. These elements, some of which normally are major elements in mantle-derived magmas, occur in extremely low concentrations in PGT grennaite. It is likely that the reported concentrations of for example Cr, Ni, and V contain a considerable amount of contamination by steel during sample preparation in the laboratory. Nonetheless, their reported concentrations are anomalously low.

A favourable geochemical factor of grennaite as a mineral deposit is the relatively low concentration of actinoids in the mineral resource. In contrast, other REE mineral deposits are commonly associated with elevated concentrations of U and especially Th (Binnemans and Jones, 2015; Chakhmouradian and Wall, 2012). For example, the agpaitic Kvanefeld deposit, which is hosted within the rock type lujavrite, is one of the world's largest deposits of U (Greenland Minerals Ltd, 2015). Monazite, one of the most important and common REE minerals, frequently contains 4–12 wt.% Th (Jordens *et al.*, 2013). The PGT grennaite domain, however, contains on average 5.57 ppm Th and 12.1 ppm U. Grennaite is relatively depleted in Th and has a low Th/U ratio of 0.461, compared to 4.75 in global average granite (Artemieva *et al.*, 2017).

Grennaite shares both mineralogical and geochemical similarities with lujavrite, a variety of agpaitic nepheline syenite with eudialyte that is described from peralkaline igneous complexes all over the world, including Lovozero (Kola Peninsula), Ilímaussaq (South Greenland), Red Wine alkaline complex (East Canada), and Pilanesberg (South Africa) (Curtis and Currie, 1981; Elburg and Cawthorn, 2017; Gerasimovsky *et al.*, 1974; Larsen and Sørensen, 1987). The signatures of compatible and incompatible trace elements in grennaite and aegirine lujavrite from Ilímaussaq show some striking similarities, such as similarly low anomalies in K, Ba, Pb, Sr, P, Ti, Li, V, Co, and Ni, and similarly elevated concentrations of incompatible elements (Figure 9). One distinction compared to most varieties of lujavrite is the relatively high concentration of Al₂O₃ and low concentration of Fe₂O₃* in grennaite, which resulted in a higher modal abundance of feldspathic minerals. While grennaite has

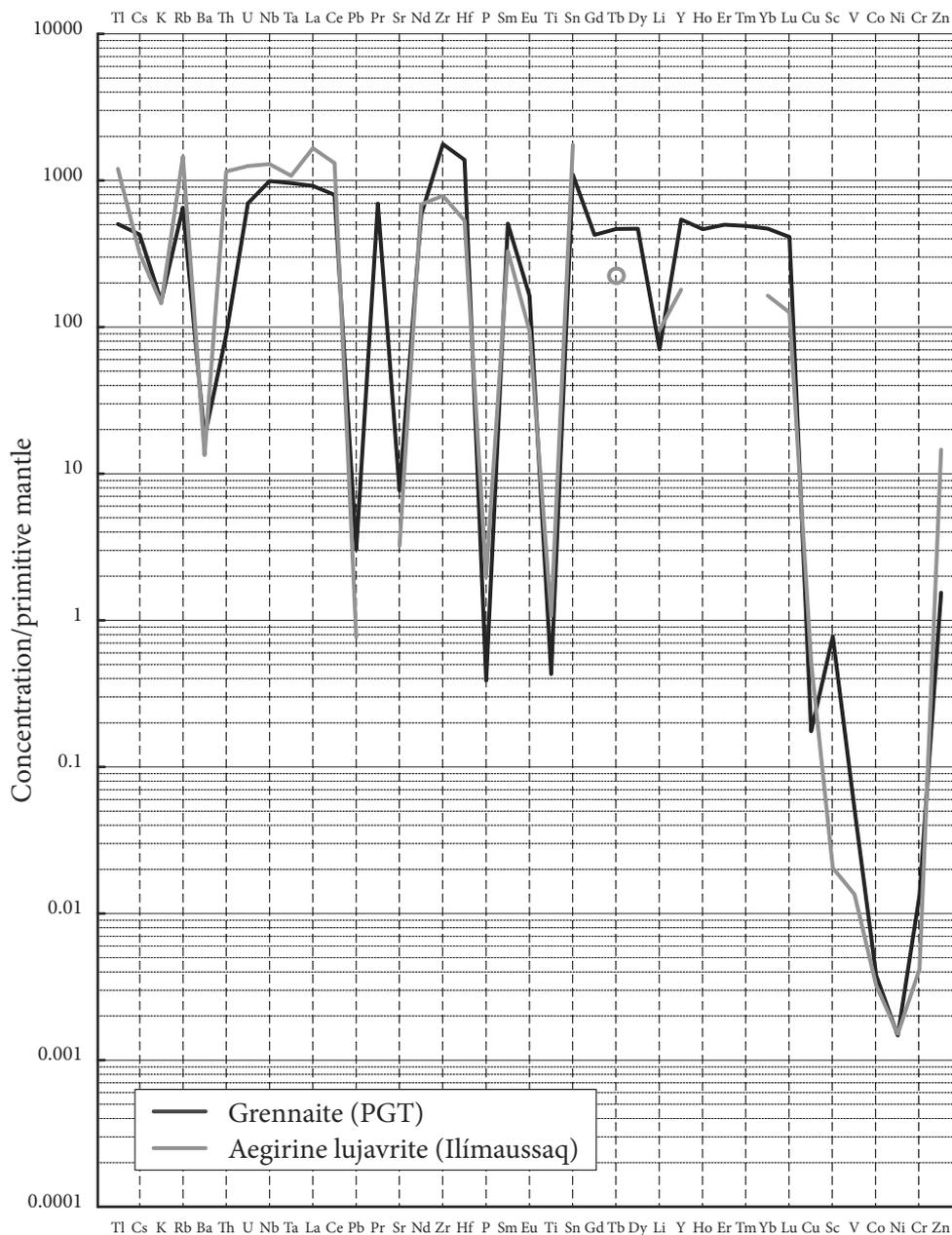


Figure 9. Grennaite (PGT) and aegirine lujavrite from Ilímaussaq (Bailey *et al.*, 2001), normalised against primitive mantle (Lyubetskaya and Korenaga, 2007). Missing data for Pr, Gd, Dy, Ho, Er, and Tm for the reported aegirine lujavrite composition. Note the low Th and high Zr and HREE content in PGT relative to aegirine lujavrite.

extremely high concentrations of alkali elements and a high Na/K mol. ratio, the relatively high concentration of Al_2O_3 reduces its Agpaitic Index, which despite an

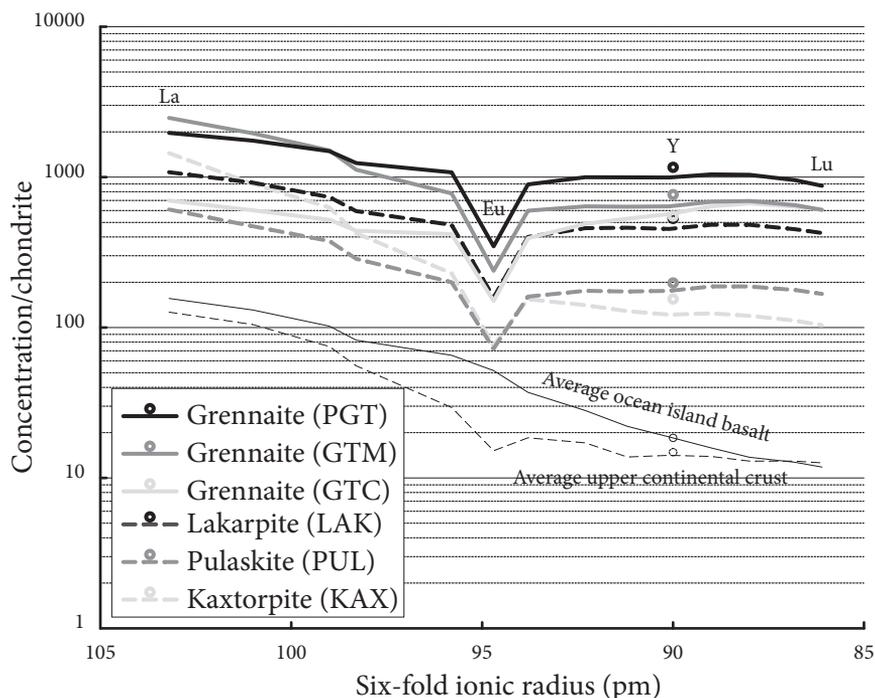


Figure 10. Chondrite-normalised REE profiles for the main rock types in Norra Kärr, compared with average upper continental crust and average ocean island basalt (Shannon, 1976; Sun and McDonough, 1989; Taylor and McLennan, 1981). Note the distinct low Eu anomaly, which is consistent across all rock types, and the relatively low La_N/Lu_N ratios.

equivalent content of alkalis is much lower than in for example hyperagpaitic lujavrite from Ílímaussaq (Khomyakov *et al.*, 2001). Grennaite is, relative to aegirine lujavrite from Ílímaussaq, richer in Zr, HREE, and Sc, but contains Th concentrations that are an order of magnitude lower.

2.3.1 Rare-earth elements

Norra Kärr has generally high concentrations of REE with a relatively high abundance of HREE, with the main share of the REE mineral deposit being hosted in various varieties of REE-rich eudialyte in grennaite (Atanasova *et al.*, 2020; Saxon *et al.*, 2015; Sjöqvist *et al.*, 2013). The most recent NI 43-101 compliant mineral resource estimate consists of 110 Mt (million tonnes) containing 0.5 wt.% total rare-earth oxide (TREO) of which 52 % is HREO (Bowell *et al.*, 2021).

Chondrite-normalised REE profiles are relatively smooth for all major rock domains (Figure 10). The La_N/Lu_N ratio, i.e. the slope of the REE profile, varies from 14 in kaxtorpite to on average 1.2 in GTC, compared to 10 and 13 for average upper

continental crust and average ocean island basalt, respectively (Sun and McDonough, 1989; Taylor and McLennan, 1981).

The REE are distributed concentrically with respect to their grade and LREE/HREE ratio in the three subdomains of grenaite, which is reflected in the composition of the EGM in the respective domains (Atanasova *et al.*, 2020; Sjöqvist *et al.*, 2013). Concentrations of REE decrease while the relative abundance of HREE increases from core to outer contact (Atanasova *et al.*, 2017; Saxon *et al.*, 2015).

All rock units in Norra Kärr contain a negative Eu anomaly, manifested by a downward spike on a chondrite-normalised REE profile (Figure 10). The Eu/Eu* ratio (Taylor and McLennan, 1985) is relatively constant throughout Norra Kärr, varying between 0.40 and 0.35.

2.4 Geochemistry: radiogenic isotopes

Radiogenic isotope geochemistry is the study of naturally-occurring radioactive decay systems. The radioactive parent isotope decays to a radiogenic daughter isotope, which accumulates over time. By measuring the relative amounts of daughter and parent isotope with a known decay constant, the radiometric age of a mineral or rock can be determined. Radioisotope systems with decay constants that are suitable for geochronology on time scales of millions to billions of years are K–Ar, K–Ca, Rb–Sr, La–Ba, La–Ce, Sm–Nd, Lu–Hf, Re–Os, Th–Pb, and U–Pb (Rollinson, 1993). Three out of eight of these parent isotope elements are rare-earth elements.

Minerals and rocks that are suitable for radiometric geochronology favour the incorporation of the parent isotope element, while rejecting the chemical element of its daughter isotope. For example, the mineral zircon readily incorporates the radioactive element U, while rejecting its daughter isotope element Pb. As a result, the majority of Pb in the zircon forms by accumulation of radiogenic daughter isotopes over geological time, rather than being derived from the common source of Pb from the environment in which the zircon initially crystallised. The age of zircon crystallisation can therefore be determined confidently by measuring the relative amounts of U and Pb isotopes, with minimal corrections for the amount of initial Pb.

On the other hand, the initial ratio of the radiogenic daughter isotope to a stable isotope of the same element can provide considerable insights into the origin of a rock. Due to variations in the relative amounts of parent and daughter isotopes in different reservoirs of the Earth, such as the lithospheric mantle and continental crust, the ratio of the radiogenic to a stable isotope changes at different rates in these various reservoirs. At given times in the Earth's development, the isotope ratios evolve along different trends in these reservoirs, which is carried on to rocks that are derived from

them. The initial isotope ratios can thus provide insights into the source reservoir of a magma, model ages of how long ago a sample was derived from an assumed mantle reservoir, magma generation from source reservoirs with different ages, and crustal contamination of mantle-derived magmas.

The initial ratio is most reliably determined in rocks and minerals with a low relative abundance of the radioactive parent isotope. In many cases, there is too much common isotope in a sample to neglect or correct for to derive the age, and there is too much parent isotope to assume the corresponding daughter isotope ratio represents the initial ratio. The isochron method, based on regression of at least two samples, is used to determine both the age (slope) and initial ratio (intercept) of the data set.

2.4.1 Available options in agpaitic rocks

Agpaitic rocks are difficult to date due to the general absence of many of the common chronometric minerals, such as zircon, baddeleyite, rutile, titanite, monazite, and apatite as well as hornblende, muscovite, and biotite (Borst *et al.*, 2019). This means that the most used modern dating techniques, *in situ* U–Th–Pb dating and Ar–Ar (and K–Ar) dating, are not widely available for geochronology of agpaitic rocks. Common chronometric minerals may, however, be present in cognate less differentiated rocks (Krumrei *et al.*, 2006).

In the vacuum of zircon, baddeleyite, rutile, titanite, monazite, and apatite, other minerals may incorporate U and Th, but there is a lack of well-characterised matrix-matched standards for these exotic minerals. Since these minerals commonly also incorporate Pb (*e.g.* EGM), measures to account for the common Pb have to be employed. Solution U–Pb geochronology on whole-rock and mineral separates is possible (Borst *et al.*, 2019). Sulphide minerals such as galena are commonly present and are well suited to determine Pb isotopes (Babiel *et al.*, 2018). Primary zircon may form as a metasomatic phase in the fenite aureole around an agpaitic intrusion (Sjöqvist *et al.*, 2017).

Although hornblende is not generally present, alkali amphibole may occur and can contain enough K for Ar–Ar (or K–Ar) geochronology (Borst *et al.*, 2019; Krumrei *et al.*, 2006). Muscovite does not occur in peralkaline rocks, but biotite may be present in less differentiated varieties. Especially biotite is sensitive to effects of slow cooling and thermal resetting and its use should be applied with care and in context of the thermochronological characteristics of the region.

The agpaitic rocks are generally rich in REE. Rare-earth elements are dominantly incorporated into Zr–Ti silicate minerals such as EGM, which also contain high concentrations of Hf (Sørensen, 1992). Thus, Lu–Hf dating is limited by relatively low

Lu/Hf ratios. On the other hand, the agpaitic rocks are generally enriched in HREE, which is beneficial for geochronology by the Sm–Nd system. The generally high concentrations of Hf and Nd hosted in minerals of various sorts is beneficial to the determination of Hf and Nd isotopes.

In theory, the La–Ba and La–Ce systems are available. Agpaitic rocks are commonly depleted in Ba whereas they are enriched in REE (Bailey *et al.*, 2001), and therefore they have high La/Ba ratios. The dating methods based on decay of La are, however, almost never used due to the low natural abundance of the radioactive isotope, which in addition has a relatively long half-life, leading to a slow accumulation of both daughter isotopes.

Concentrations of Re are too low to consider Re–Os geochronology.

The high chemical mobility of Rb and Sr, as well as K and Ca, especially in hydrothermal systems, makes the Rb–Sr isotope system prone to late- or post-magmatic disturbances (Blaxland, 1977; Borst *et al.*, 2019). Additionally, agpaitic rocks are commonly characterised by low concentrations of Sr and the initial Sr ratio is therefore prone to being distorted by contamination (Sørensen, 1997). However, the concentrations of Rb and Rb/Sr ratios are generally high. Therefore, *in situ* Rb–Sr geochronology, which allows the dating of selected undisturbed mineral domains, is a new technique with potential for geochronology of agpaitic rocks (Hogmalm *et al.*, 2017; Zack and Hogmalm, 2016).

2.4.2 Radiogenic isotope data for Norra Kärr

The investigations of radiogenic isotopes in Norra Kärr are discussed in detail in Chapter 3 and in appended scientific papers (Sjöqvist *et al.*, 2017, 2020). Below is a compilation of the work carried out to date:

- Von Eckermann (1968): K–Ar dating of grennaite and surrounding TIB granitoid.
- Blaxland (1977): Rb–Sr dating of a collection of whole-rock samples and mineral separates.
- Bibikova *et al.* (1980): Pb–Pb dating, four samples of eudialyte and feldspar.
- Patchett *et al.* (1981): Lu–Hf isotopes, a single eudialyte sample.
- Kramm and Koark (1988): Pb isotopes of galena.

- Ulf Bertil Andersson (unpublished data): U–Pb dating of zircon from the northern outcrop in Lakarp; whole-rock Sr and Nd isotopes.
- Sjöqvist *et al.* (2014): Ar–Ar dating of alkali amphibole from lakarpite, biotite from fenite, and muscovite from an ultramylonite in the region.
- Sjöqvist *et al.* (2017): U–Pb dating of zircon from fenite and granite; Hf isotopes of zircon and eudialyte.
- Axel Sjöqvist and Tom Andersen (unpublished data): Pb isotopes of galena.
- Fazic (2018): *in situ* Rb–Sr dating of biotite in unfenitised granite from Lakarp.
- Sjöqvist *et al.* (2020): Sm–Nd dating and Nd isotopes of eudialyte from a pegmatoid vein.

“

At the heart of science is an essential balance between two seemingly contradictory attitudes — an openness to new ideas, no matter how bizarre or counterintuitive they may be, and the most ruthless skeptical scrutiny of all ideas, old and new.”

—Carl Sagan (1997)

3

Rationale and Summary of Papers

THE GLOBAL SUPPLY of rare-earth elements so far in the 21st century has been dominated by Chinese mining and production. In 2010, while producing 97 % of the world's rare-earth element supply, China imposed stringent export restrictions on these elements. As a result, prices for rare-earth elements soared (ERECON, 2015). Enterprises, largely junior exploration companies, were scouring the surface of the Earth for promising deposits of minerals that contain the sought-after elements. A large number of geological occurrences, many hosted by carbonatite and alkaline intrusions, were swiftly evaluated, spurred on by an abundance of media hype and financial speculation.

The REE mineral resource in Norra Kärr is hosted by minerals of the eudialyte group. These are non-conventional ore minerals and REE have not been produced by commercial mining of eudialyte (Jordens *et al.*, 2013). Norra Kärr is, so far, also the only occurrence of agpaitic nepheline syenite in mainland Europe that is known to contain a significant REE mineral deposit (Goodenough *et al.*, 2016). This merits research into the petrogeny, composition, and development of agpaitic rocks in general and EGM in particular, which are an important potential mineral resource of REE for the EU.

3.1 Summary of papers

Paper I

Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Erambert, M., Ek, M., Leijd, M. (2013). Three Compositional Varieties of Rare-Earth Element Ore: Eudialyte-Group Minerals from the Norra Kärr Alkaline Complex, Southern Sweden. *Minerals*, 3, 94–120.

While the Norra Kärr mineral deposit was showing good bulk grades, it had so far only been concluded that “eudialyte may contain significant amounts of rare-earth elements” (Reed, 2011, p. 5). The chemical composition of eudialyte-group minerals from Norra Kärr had been studied previously in various detail (Fryer and Edgar, 1977; Patchett *et al.*, 1981; Schilling *et al.*, 2011; Törnebohm, 1906). The eudialyte analysed by Mauzelius (Törnebohm, 1906) contained high total concentrations of rare-earth elements (6.87 wt.% TREO), whereas Schilling *et al.* (2011) found much lower concentrations (1.5 wt.% TREO). The apparent inconsistency in reported REE concentrations in EGM from Norra Kärr was the cause of our investigation to systematically analyse EGM grains from both a lithological and geographical spread.

Eudialyte-group mineral grains were collected from samples taken at 18 spread-out locations in Norra Kärr. They were analysed both by quantitative SEM-EDS (Department of Earth Sciences, University of Gothenburg) and EMP-WDS (Department of Geosciences, University of Oslo). A comparison of the results obtained by both methods showed good agreement, meaning that after careful calibration, SEM-EDS is an adequate method to analyse also complex minerals such as EGM in reconnaissance studies and preliminary work in research. Where analyses with higher confidence are required, analytical protocols have been developed for EMP to analyse eudialyte-group minerals (Andersen *et al.*, 2010; Atanasova *et al.*, 2015).

From our dataset we showed there are apparently (at least) three varieties of eudialyte-group minerals in Norra Kärr, forming a trend with different compositions:

1. Fe-rich, REE-poor,
2. Fe-Mn intermediate, Y-rich,
3. Mn-rich, LREE-rich.

Of these, types 2 and 3 are hosted in two subunits of the grennaite and are the most abundant type of EGM. Type 1 occurs in a variety of lakarpite, prominently exposed in an outcrop centrally in the complex. The compositional variety and types of

eudialyte from Norra Kärr have been further investigated and widened by Atanasova *et al.* (2020, 2017).

From observations of mineral modal abundances together with our analyses, it can be asserted that EGM are the main REE-bearing mineral phase in grennaite. The EGM variety that is most commonly sampled in the field by mineral collectors or visiting researchers (type 1) is the least representative for the mineral deposit in terms of REE content.

Author's contribution

Concept and design: **Sjöqvist**, Leijd, Cornell, and Andersen

Material collection: **Sjöqvist** and Leijd

Analytical work: **Sjöqvist**, Cornell, and Ek (SEM); **Sjöqvist** and Erambert (EMP)

Data analyses and interpretation: **Sjöqvist**, Cornell, and Andersen

Computer graphics: **Sjöqvist**, Andersen, and Leijd

Original draft: **Sjöqvist**, Andersen, and Cornell

Proofreading and edit: **Sjöqvist**, Cornell, and Andersen

Paper II

Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Christensson, U.I., Berg, J.T. (2017). Magmatic age of rare-earth element and zirconium mineralisation at the Norra Kärr alkaline complex, southern Sweden, determined by U–Pb and Lu–Hf isotope analyses of metasomatic zircon and eudialyte. *Lithos*, 294–295, 73–86.

The timing of magmatic intrusion of the Norra Kärr alkaline complex has been a point of debate since Törnebohm's first presentation of the rocks in 1905 (Munthe, 1905). Törnebohm (1906, pp. 32–33) suggested that the rocks “could not be older than Early Jurassic but possibly younger”, whereas De Geer found a Precambrian age more likely (Munthe, 1905). Gavelin (1912) argued for a Jotnian age, but Geijer (1922) placed it among the sub-Jotnian intrusive rocks alongside the rapakivi granites. In his doctoral dissertation about Norra Kärr, Adamson (1944) was brief about the intrusion age, but stated it had to be younger than the regional deformation in the “Gothian” granite it intruded. Von Eckermann (1960) argued for an age similar to the Alnö carbonatite, which he had then dated to 562 Ma by the K–Ar method (Von Eckermann and Wickman, 1956).

Radiometric ages of minerals and rocks from Norra Kärr have not painted a more coherent picture than the above-mentioned relative ages. Von Eckermann (1968) presented a K–Ar date of 1020 Ma, which he suggested as the intrusive age. Koark (1969) on the other hand suggested this could represent the age of a metamorphic overprinting event, which he had argued for in contradiction to Von Eckermann, who did not believe that Norra Kärr had been metamorphosed. Further on, an imprecise

feldspar and eudialyte Pb–Pb isochron of 1840 ± 300 Ma was published by Bibikova *et al.* (1980). Kramm and Koark (1988) derived a galena Pb isotopic age of 1525 Ma (approximate error of ± 100 Ma).

Blaxland (1977, p. 5) presented an imprecise whole-rock Rb–Sr isochron age of 1580 ± 62 Ma (2σ), for which “the scatter about the best-fit line exceeds that to be expected from analytical uncertainty”. In addition, he showed that ages of mineral separates fell on reference age lines between 1250 and 1040 Ma, which he argued was evidence for isotopic disturbance after the igneous event, probably as a result of partial Sveconorwegian metamorphism. Despite this, Blaxland’s disturbed age persisted as the preferred age in the literature.

Our aim was to determine the age of the igneous event at Norra Kärr with high confidence, which we wanted to achieve by conventional *in situ* zircon U–Pb dating and Hf isotope analyses. However, agpaitic rocks are notoriously difficult to date by conventional methods (Borst *et al.*, 2019). Largely this is due to the general absence of common chronometric minerals such as zircon, baddeleyite, titanite, monazite, and mica. Another factor, related to alkaline rocks in general, is the preponderance for late-stage fluids to cause widespread alteration and remobilisation of elements.

It is important to be able to interpret the processes that gave rise to zircon growth in order for the obtained radiometric age to bear any meaning. Since the definition of an agpaitic rock is that it should not contain primary zircon (Sørensen, 1997), dating zircon from the agpaitic rocks themselves is potentially problematic if the aim is to determine the timing of the igneous event. Zircon is a common secondary mineral after EGM, both in silica under- and oversaturated systems (*e.g.* Estrade *et al.*, 2018; Van de Ven *et al.*, 2019). Given the suggested metamorphism in Norra Kärr (Atanasova *et al.*, 2017; Blaxland, 1977; Koark, 1969, 1960; Kramm and Koark, 1988), it would have been highly speculative to assert that all zircon in the agpaitic nepheline syenite, including the majority found in secondary replacement assemblages, formed exclusively during syn- or late-magmatic processes and not during possible later events.

Rather, our approach was to focus on the syn- to late-magmatic metasomatic alteration (finitisation) of the country rock granite. Inspection of finitised granite with a short-wave ultraviolet light revealed abundant and large yellow-fluorescent zircon (Figure 11). We hypothesised that fluids expelled from the alkaline magma had either isotopically reset existing granitic zircon or formed new metasomatic zircon. The timing of this process can be interpreted unambiguously and the zircon would be less likely affected by a later metamorphic event.

Zircon crystals were separated and mounted in epoxy grain mounts, but represented

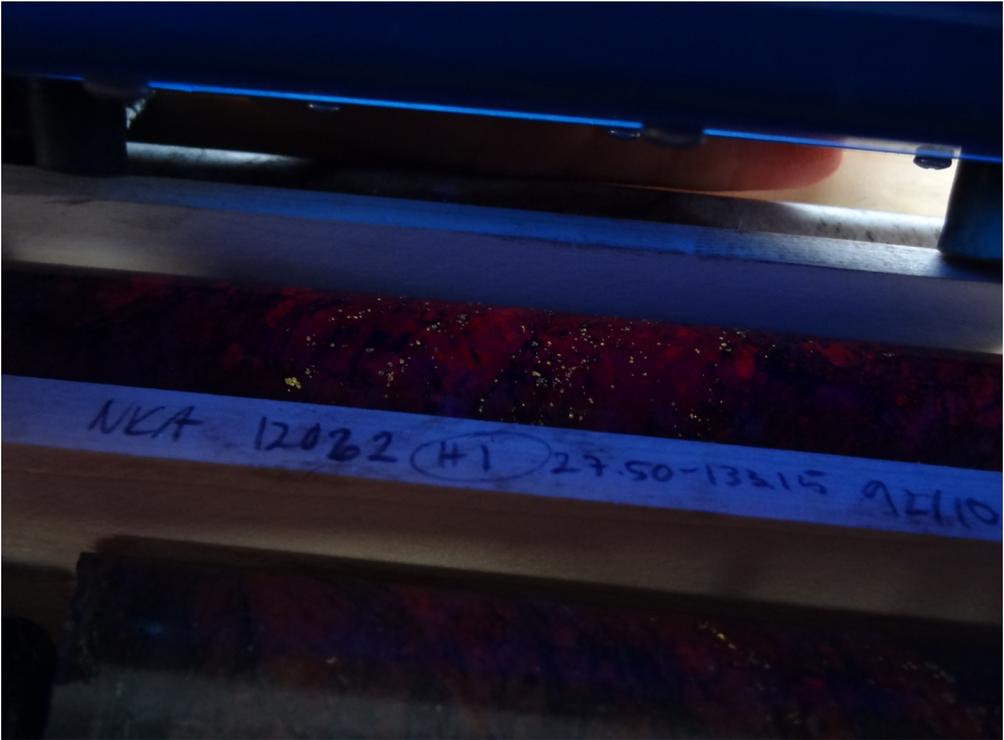


Figure 11. Abundant yellow-fluorescent zircon and orange-fluorescent albite in an intensely fenitised vein in the western hanging wall of Norra Kärr. Photograph of drill core illuminated with short-wave ultraviolet light.

only fragments of larger zircon crystals. Therefore, we also prepared polished rock slabs embedded in epoxy to preserve textural information. Two fenite samples were analysed for U–Pb and Hf isotopes by LA-MC-ICP-MS (Department of Geosciences, University of Oslo) on two separate occasions. The zircon U–Pb ages obtained from both samples were statistically within error and a pooled concordia intercept age of all data gave 1492 ± 8 Ma (2σ). The $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic composition of the zircon in fenite is significantly more mantle-like than zircon in unaltered granite, which has a typical composition reflecting Svecofennian crustal evolution since 1.9 Ga. The fenite Hf overlaps the Hf signature measured in Lu-poor eudialyte. This observation precludes a crustal origin for the Hf in fenite zircon and is consistent with a process that mobilised Hf from the agpaite magma incorporated in new zircon in the fenite. Therefore, we could confidently interpret the fenite zircon U–Pb age to record the timing of syn- to late-magmatic events in the Norra Kärr alkaline complex.

Our efforts to extract zircon from the main agpaite rock units in Norra Kärr were unsurprisingly unfruitful, with the exception of zircon xenocrysts in lakarpite, which displayed a rounded habit, possibly as if they were chemically abraded and partially

dissolved by the alkaline magma. Their ages are convoluted into 1.5–1.6 Ga and 1.8–2.0 Ga groups with the addition of one Archaean (2.5 Ga) grain.

There are no immediately coeval corresponding rocks exposed at the surface near Norra Kärr. The intrusion is coeval with rapakivi rocks in middle Sweden and western Finland. We suggest that there are Mesoproterozoic lower-crustal intrusions beneath the Norra Kärr magmatic conduit. The 1.8–2.0 Ga group most probably reflects rocks belonging to the Svecofennian crust and Transscandinavian Igneous Belt.

There is no known Archaean crust in this part of the Baltic Shield, although Archaean detrital zircons are not unusual in sedimentary rocks of the Bergslagen region and xenocrystic zircon cores older than 2.44 Ga are known from the 1855 ± 6 Ma (2σ) Finspång augen gneiss and a 1793 ± 5 Ma (2σ) garnet-cordierite gneiss from Karlskoga (Andersson *et al.*, 2006 and references therein) located approximately 100 km NE and 140 km N from Norra Kärr, respectively.

Author's contribution

Concept and design: **Sjöqvist** and Cornell

Material collection: **Sjöqvist**, Cornell, Christensson, and Berg

Analytical work: **Sjöqvist**, Cornell, and Christensson (SEM); **Sjöqvist**, Cornell, Christensson, and Andersen (LA-MC-ICP-MS)

Data analyses and interpretation: **Sjöqvist**, Cornell, and Andersen

Computer graphics: **Sjöqvist** and Berg

Original draft: **Sjöqvist**

Proofreading and edit: **Sjöqvist**, Cornell, and Andersen

Paper III

Sjöqvist, A.S.L., Zack, T., Honn, D.K., Baxter, E.F. (2020). Modification of a rare-earth element deposit by low-temperature partial melting during metamorphic overprinting: Norra Kärr alkaline complex, southern Sweden. *Chemical Geology*, 545, 119640.

It is commonly acknowledged that rare-earth element mineral deposits globally show a tendency to have been formed by multiple geological processes. In the case of deposits hosted within alkaline igneous rocks, the first mineralisation is formed by primary magmatic processes, which later can be modified by late-magmatic or post-magmatic (fluid-driven) processes. Notably, the world's prime and largest REE resource at Bayan Obo mine in China was shaped by ore-forming phases from its origination at 1.3 Ga followed by multiple modifications until 0.4 Ga (Smith *et al.*, 2015).

The principal mineral resource domain of Norra Kärr is characterised by EGM-rich pegmatoid veins and dykes that occur in a fine-grained nepheline syenite matrix that

centrally exhibits a recrystallised or migmatised texture, called the Pegmatitic Grennaite domain (PGT) and Migmatitic Grennaite domain (GTM) in the nomenclature and domaining of the rare-earth mineral deposit (Bowell *et al.*, 2021; Saxon *et al.*, 2015). Eudialyte-group minerals from these domains are rich in rare-earth elements (Sjöqvist *et al.*, 2013).

The timing of magmatic activity in Norra Kärr is inferred from the dating of metasomatic zircon that formed during fenitisation in the country rock at 1.49 Ga (Sjöqvist *et al.*, 2017). The different nepheline syenite varieties are dominated by pervasive metamorphic foliation, which in central parts of the complex is folded (Atanasova *et al.*, 2017; Bowell *et al.*, 2021; Koark, 1960; Sjöqvist *et al.*, 2013). The mineralised pegmatoids range in size from centimetre-wide leucocratic “schlieren” subparallel to the dominant foliation to decimetre-wide medium- to coarse-grained pegmatoid veins that cross-cut foliation to very coarse-grained pegmatoid dykes or pods intersected over more than 10 metres in drill cores.

The cross-cutting relationship between the foliation in the host nepheline syenite and the eudialyte-rich pegmatoids implies that the latter are younger than the age of fabric. This suggests that rare-earth elements were remobilised into the pegmatoids during an event that post-dates the age of fabric in the host nepheline syenite. To understand the timing of REE redistribution in Norra Kärr, we wanted to determine the absolute age of pegmatoid formation.

To determine the age, we built upon an established micromilling method for sampling of plagioclase for Sr isotope analyses (Charlier *et al.*, 2006) and adapted it for microsampling of EGM for Nd isotope analyses by ID-TIMS. One pegmatoid sample (NK7) was chosen from a previously compiled collection of samples from all lithology types in Norra Kärr, mainly due to its clear cross-cutting relationship with the host rock, its internally undeformed structure, and large EGM crystals with clear zoning patterns visible in thin section.

One large EGM crystal with sector and oscillatory zoning was characterised in detail by backscattered electron imaging and qualitative analyses for mineral identification by SEM (Department of Earth Sciences, University of Gothenburg). Subsequently, the different crystal domains were analysed by LA-ICP-MS (Department of Earth Sciences, University of Gothenburg) to pre-characterise the range and distribution of Nd concentrations and Sm/Nd ratios in the crystal in preparation for destructive sampling by micromill. Based on the Nd concentrations and theoretical precision of the Nd isotope analyses by ID-TIMS, a minimum required sample volume was calculated ahead of sampling.

The eudialyte was sampled in six places by micromilling inside a water droplet, which was pipetted out each time and transferred to a beaker for routine small-aliquot Nd isotope analysis by ID-TIMS (Department of Earth Sciences, Boston University). Two of the samples showed signs of contamination by secondary fluorbritholite-(Ce), which could be recognised by validation against the SEM BSE images and LA-ICP-MS data. The remaining four points contained enough spread in $^{147}\text{Sm}/^{144}\text{Nd}$ ratio to produce an internal isochron age of 1144 ± 53 Ma (2σ). This age is well in line with an uninterpreted Ar–Ar stepheating plateau age of 1148 ± 5 Ma (2σ) derived from arfvedsonite from Norra Kärr (Sjöqvist *et al.*, 2014). The ϵ_{Nd} of the Norra Kärr alkaline complex, back-calculated from 1.14 Ga to 1.49 Ga with a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.165, is approximately 1.65. This is consistent with a mantle source for the alkaline magma, as also indicated by the 6.58 ϵ_{Hf} obtained from zircon and eudialyte (Sjöqvist *et al.*, 2017).

The cross-cutting pegmatoid veins are approximately 350 million years younger than the age of magmatic activity and fenitisation of the surrounding granite (Sjöqvist *et al.*, 2017). Our interpretation is that the pegmatoids formed by low-temperature partial melting of the agpaitic nepheline syenite during the 1.1–0.9 Ga Sveconorwegian orogeny. This low-temperature partial melting of agpaitic nepheline syenite has never before been confirmed by direct geochronology of pegmatoid veins. The method we developed to directly date eudialyte has a wide application for geochronology of occurrences of EGM and other REE-rich minerals by micromill sampling and ID-TIMS.

Author's contribution

Concept and design: **Sjöqvist**, Zack, and Baxter

Material collection: **Sjöqvist**

Analytical work: **Sjöqvist** (SEM); **Sjöqvist** and Zack (LA-ICP-MS); **Sjöqvist**, Honn, and Baxter (ID-TIMS)

Data analyses and interpretation: **Sjöqvist**, Zack, and Baxter

Computer graphics: **Sjöqvist**

Original draft: **Sjöqvist**

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Paper IV

Hogmalm, K.J., Zack, T., Karlsson, A.K.-O., **Sjöqvist, A.S.L.**, Garbe-Schönberg, D., 2017. *In situ* Rb–Sr and K–Ca dating by LA-ICP-MS/MS: an evaluation of N₂O and SF₆ as reaction gases. *Journal of Analytical Atomic Spectrometry*, 32, 305–313.

Radiometric dating methods rely on the radioactive decay of a parent isotope to a daughter isotope with a known half-life, for example decay of ^{147}Sm to ^{143}Nd with a half-life of 106.2 billion years. By measuring the amount of parent and daughter

isotope in a mineral, the amount of time that has passed since it formed can be calculated.

During α decay the parent isotope expels a helium atom and thus parent and daughter isotope have different masses and can be analysed *in situ* without overlap by conventional LA-ICP-MS. On the other hand, during β decay the parent isotope expels an electron and thus the parent and daughter isotopes have equal mass. These isotopes would overlap and be indistinguishable during LA-ICP-MS analysis and therefore require chemical separation prior to analysis, meaning that *in situ* measurements of β decay systems, such as Rb–Sr, in minerals have been impossible.

Advancement in ICP-MS technology has made online chemical separation possible, by placing a gas-reaction chamber between two mass filters. After the plasma, the ions are passed into a reaction chamber. The chamber can be either under vacuum or filled with a gas. The first mass filter allows targeted ions to enter the chamber and react with the gas and form charged polyatomic ions. By choosing a reaction gas that has a high selectivity for either parent or daughter isotope, the reaction product can be separated and analysed free from overlap.

Zack and Hogmalm (2016) used this apparatus to separate strontium ions from rubidium ions by reaction with O₂ gas, making *in situ* Rb–Sr dating possible. While selective, <10 % of the total Sr⁺ ions that enter the gas chamber react with the O₂ gas to form SrO⁺, leaving room for improvement to the analytical sensitivity of the method.

In this study, the method was further developed by evaluating other reaction gasses that had previously shown similar selectivity for Rb and Sr. Analytical conditions were optimised for both N₂O and SF₆ gas, which resulted in reaction rates of >85 % and >70 % Sr, respectively. The sensitivity for Sr reaction products with these gasses is approximately 10 fold and 8 fold compared to O₂ gas, respectively, allowing analyses with higher spatial resolution and better analytical precision.

Using SF₆ as a reaction gas combined with H₂ gas makes it possible to separate K from Ca, and to analyse radiogenic Ca without overlap from Ar ions in the plasma. Since the initial ratio of common Ca practically is a constant, this allows single-spot dating of potassic minerals without the isochron method. Simultaneous *in situ* measurements of Rb–Sr and K–Ca isotopes are possible (Sjöqvist *et al.*, 2018), resulting in a geochronometer that is analogous to the U–Pb system.

The Rb–Sr and K–Ca geochronometers are especially applicable to K- and Rb-rich minerals, which are abundant in many varieties of alkaline igneous rocks. Petrochronology by *in situ* Rb–Sr dating has been applied by Ranjer (2016) and

Eliasson (2018) at two Swedish localities of alkaline igneous rocks. The method is also applicable within the field of thermochronology, for example by *in situ* dating of biotite, which has a Rb–Sr closure temperature of 300 ± 50 °C (Harrison and McDougall, 1980). An exploratory study based on *in situ* Rb–Sr biotite thermochronology has been carried out in the region surrounding Norra Kärr by Fazic (2018).

Author's contribution

Concept and design: Hogmalm, Zack, and Karlsson (Rb–Sr); **Sjöqvist** and Zack (K–Ca)

Material collection: Karlsson and Garbe-Schönberg

Analytical work: Hogmalm, Zack, and Karlsson (Rb–Sr); Zack and **Sjöqvist** (K–Ca)

Data analyses and interpretation: Hogmalm, Zack, and Karlsson (Rb–Sr); **Sjöqvist** and Zack (K–Ca)

Computer graphics: Hogmalm

Original draft: Hogmalm

Proofreading and edit: Hogmalm and Zack

Paper V

Sjöqvist, A.S.L., 2019. The Tale of Greenlandite: Commemorating the Two-Hundredth Anniversary of Eudialyte (1819–2019). *Minerals*, 9, 497.

The mineral eudialyte was first described, analysed, and named by Friedrich Stromeyer in 1819. However, Stromeyer mentioned that this new mineral is deceptively similar to a red garnet variety from Greenland (Stromeyer, 1819). The first two chemical analyses of that garnet, over a decade earlier, reported a zirconium content comparable to eudialyte (Gruner, 1803; Trommsdorff, 1801). Scientists that came after Stromeyer speculated whether the Greenlandic garnet and eudialyte could have been the same mineral (Weiss, 1829) or right-out claimed that this was the case (Rammelsberg, 1841). Having accepted these later claims at face value, I also included the same statement in my Licentiate of Philosophy dissertation (Sjöqvist, 2015).

Stromeyer's eudialyte specimen was collected by Karl Ludwig Giesecke during a dramatic expedition to Greenland 1806–1813 (Giesecke, 1878), and he was in fact the first mineralogist to visit and systematically study the Greenlandic coast (Johnstrup, 1878). For this reason, I became fascinated by the unknown origin of this earlier Greenlandic garnet, said-to-be eudialyte, collected and studied before Giesecke had visited Greenland.

I conducted a systematic review of the historical literature, written in German, French, English, and Danish, with some minor lingual input from colleagues and acquaintances. The literature review was overwhelmingly facilitated by the efforts of

institutions that digitalise old scientific literature and make it publicly available online after the expiry of copyrights. This allowed me to query databases of historical literature for keywords, which immensely reduced the body of literature that had to be scrutinised.

The article contains a chronological description of the relevant events leading up to the discovery of eudialyte and brief biographical entries for the main scientists that played a role. My research shows that the origin of the Greenlandic garnet that was studied by European mineralogists and chemists, which later turned out to be aesthetically similar to and confused with eudialyte, was probably brought to the Danish colonial town of Godthaab (Nuuk) by Greenlandic reindeer hunters. This area does not host any peralkaline igneous complexes with agpaitic minerals, so the Greenlandic garnet cannot be eudialyte.

Author's contribution

*The concept and design, research and interpretation, computer graphics, original draft, proofreading and edit were independently carried out by **Sjöqvist**.*

“

I think, nevertheless, that it is justified to look upon the zirconium-rich alkaline districts as having certain genetical features in common, distinguishing them from the carbonate-rich alkaline districts and from districts showing neither of these chemical characteristics.”

—Olge Jungstedt Adamson (1944)

4

A Recipe for an Agpaitic Magma

THE ORIGIN OF alkaline igneous rocks in general has been a longstanding problem in petrology, which this thesis does not aim to solve. Additionally, there is not a common origin for all alkaline rocks (Sørensen, 1974), which form from various parental magmas and along various differentiation paths. The purpose of this chapter is to synthesise the findings of my research into a quasi-conceptual model for the mode of formation of extremely differentiated agpaitic magma, based on associations I have made by studying the rocks at Norra Kärr.

Agpaitic rocks are commonly found in close connection with other igneous rocks, either in igneous complexes or igneous provinces. They frequently represent the final stage of magma differentiation in an igneous complex or province, for example illustrated by peralkaline agpaitic pegmatoids of the Langesundsford in the Permian Oslo Rift (Andersen *et al.*, 2010) and by the emplacement of the agpaitic magma in the Ilímaussaq alkaline complex after augite syenite and alkali granite during the late stages of activity in the Gardar Province (Upton, 2013). The provincial association of igneous rocks provides insight into the tectonic regime and inferred parental melts and differentiation processes at depth that gave rise also to the most evolved magmas.

Norra Kärr is a special case. It represents an intrusion of apparently extremely

differentiated magma, which seems to occur in absolute isolation without obvious nearby candidates of consanguineous rocks in space or time. That poses a problem for any model that aims to explain the occurrence of agpaitic nepheline syenites at Norra Kärr by association with other igneous rocks and tectonic events.

4.1 General model for the origin of agpaitic rocks

The definition of agpaitic rocks puts no geochemical limitations on their bulk compositions (Marks and Markl, 2017; Sørensen, 1997, 1960). Nevertheless, most varieties of agpaitic rocks have in common that they are highly peralkaline. Therefore, the processes that can generate and amplify peralkalinity in a magma are of key interest to understanding the formation of agpaitic rocks.

One such process, which is often invoked, is the so-called “plagioclase effect” (Bowen, 1945). Whereas many common Al-rich minerals incorporate alkali elements in equal molar amounts (*e.g.* alkali feldspar, feldspathoids, biotite), the mineral end-member anorthite binds two Al for each Ca without also incorporating alkali elements. Thus, fractional crystallisation of the anorthite component in plagioclase or ternary feldspar increases the ratio of alkali elements to Al in the residual magma. Extensive fractional crystallisation of plagioclase feldspar from a magma with a sufficient amount of Ca in relation to Al and alkali elements has the potential to produce a residual peralkaline magma, eventually. In the cases where the residual magma does become peralkaline, continued fractional crystallisation of alkali feldspar can amplify the peralkalinity (Giehl *et al.*, 2013).

This concept makes it tempting to associate peralkaline igneous complexes with occurrences of large amounts of sequestered plagioclase in the form of anorthosites. In South Greenland, “big feldspar dykes” (BFD) are dolerite dykes that contain abundant plagioclase megacrysts and anorthosite xenoliths. They belong to a late phase of magmatic activity in the Gardar Province and are regionally and temporally associated with alkaline complexes, including Ilímaussaq, which itself also contains some rare xenoliths of anorthosite (Bridgwater, 1967; Bridgwater and Harry, 1968; Upton, 2013). Further, the eastern Canadian Shield is rich in massif-type anorthosites, which also are regionally and temporally associated with alkaline complexes, including the agpaitic Red Wine alkaline complex in Labrador (Curtis and Currie, 1981). The connection between (agpaitic) peralkaline complexes and anorthosites could perhaps also be explained by large-scale tectonics (Halama *et al.*, 2002) rather than the anorthosites representing a plagioclase cumulate precursor to the peralkaline rocks.

The mode of formation of anorthosites, the composition and origin of their parental magmas, and timing of their emplacement are non-trivial questions that remain a

petrological problem (Ashwal, 1993). It is not necessary to expand the topic at hand with the specifics of the anorthosite petrology, more than to reiterate that the apparent association between peralkaline igneous rocks and anorthosites, irrespective of the process, is interesting.

The processes involved in the differentiation of a magma leave imprints on the geochemical composition of the derived igneous rocks. The concentrations of chemical elements in minerals that crystallise from the magma are controlled by the composition of the magma and the mineral/melt partition coefficients for each element into a particular mineral². Some chemical elements are preferentially incorporated into the crystallising minerals, due to their high mineral/melt partition coefficients. These are called compatible elements and during crystallisation their concentration in the residual magma is depleted. On the other hand, incompatible elements have low mineral/melt partition coefficients and are disadvantageously incorporated into crystallising minerals. The incompatible elements are increasingly concentrated in the magma with progressive crystallisation. Depending on the composition of the magma and the species of minerals that are formed, different elements may behave as compatible and incompatible at different stages of magma differentiation. Therefore, by making observations about the relative and absolute abundances of the chemical elements and deducing which behaved as compatible and incompatible elements, inferences can be made about the crystallisation history of the magma-derived rocks.

The broader family of agpaitic nepheline syenites is subdivided based on the inferred parental magma compositions. These are agpaitic rocks with an inferred basaltic association (Larsen and Sørensen, 1987; Upton, 1974) or nephelinitic association (Kramm and Kogarko, 1994). Both are capable of producing eudialyte-rich peralkaline nepheline syenite, but these are defined by markedly different geochemical characteristics as a result of their respective fractionation trends. Rare silica-oversaturated agpaitic rocks (Estrade, 2014), on the other hand, show geochemical similarities with the group of inferred basaltic association, but will not be discussed in further detail here.

The distinction between an inferred alkali basaltic or nephelinitic parental magma is, at a glance, made by evaluating the Eu anomaly. As a result of the high partition coefficient of divalent Eu in plagioclase, fractional crystallisation of plagioclase causes the Eu/Eu^* to decrease in the residual magma and thus produces a “negative Eu anomaly” (Weill and Drake, 1973). Plagioclase also has a high partition coefficient for

² Mineral/melt partition coefficients are evaluated by querying the GERM Partition Coefficient (Kd) Database, made available by EarthRef.org.

Sr. Therefore, peralkalinity caused by extensive fractional crystallisation of plagioclase under normal conditions of oxygen fugacity would be accompanied by a low Eu/Eu^* value and a low concentration of Sr.

Agpaitic rocks are generally rich in Ga and therefore have high Ga/Al ratios (Marks and Markl, 2017). This characteristic is shared with A-type granites (Whalen *et al.*, 1987). The high Ga/Al ratio of agpaitic rocks disfavours hypotheses that involve fractional crystallisation of spinel to increase the alkalinity of the residual magma, since Ga partitions strongly into spinel whereas it is slightly incompatible in plagioclase (Malvin and Drake, 1987).

It is inferred that the agpaitic nepheline syenites with low Eu/Eu^* evolved from a basaltic magma from which a substantial fraction of plagioclase has been removed (Larsen and Sørensen, 1987; Sørensen, 1997). Nephelinite magma does not tend to crystallise much plagioclase. Therefore, it is preferred as the parental magma for agpaitic nepheline syenites that lack a Eu anomaly, such as Khibina and Lovozero (Kramm and Kogarko, 1994).

In addition to a low Eu/Eu^* ratio, the rocks in for example Ilímaussaq also contain extraordinarily low concentrations of compatible elements like Ba, Sr, P, Co, Cu, Ni, Sc, V, Cr, and Mg (Bailey *et al.*, 2001), which is suggested to have taken place by fractional crystallisation of other minerals like olivine and Fe-Ti oxide in a basaltic magma chamber (Sørensen, 1997). If it were assumed that the Ilímaussaq magma evolved by conventional fractional crystallisation of an alkali basalt, the observed enrichment in incompatible elements would require 98 % crystallisation of the parental basaltic magma, amounting to a gabbroic cumulate of approximately 10000 km^3 (Larsen and Sørensen, 1987). Additionally, the most evolved lujavrites may have crystallised after 99 % fractional crystallisation of augite syenite (Bailey *et al.*, 2001). It is worth stating, though, that the precise origin of the flagship of agpaitic nepheline syenites, the well-studied Ilímaussaq alkaline complex, is still contentious (Upton, 2013).

While the agpaitic rocks in Khibina and Lovozero are similar to those found in Ilímaussaq in many respects, they also display large differences. Similar to Ilímaussaq, their chemical compositions are peralkaline, highly enriched in LILE and HFSE, and strongly depleted in Ni, Cr, Co, and Sc, however they lack a negative Eu anomaly and are also relatively rich in Sr (Kramm and Kogarko, 1994). Additionally, both Khibina and Lovozero are rich in P and contain economically significant deposits of apatite (Semenov, 1974). Therefore, they became peralkaline by another process that did not involve plagioclase crystallisation, which is still not well understood. Possibly, the peralkalinity of these magmas could be traced back to an alkali-metasomatised mantle source (Markl *et al.*, 2010).

The formation of nepheline syenite by fractional crystallisation of alkali basaltic magma via augite syenite is for example illustrated in the Older giant dyke complex (OGDC) on Tuttutooq island, South Greenland, which is 500–600 m wide and can be followed for 20 km. The chilled margin consists of an alkali basalt of hawaiitic composition. The marginal facies consist of gabbro and ferro-syenogabbro. The central unit, up to 300 m wide, shows a gradual transition from augite syenite in the west, through pulaskite and foyaite, to peralkaline sodalite syenite in the east. Due to presumed block rotation of the dyke, the west to east traverse provides a diagonal section through the magma chamber. The gradually increasingly alkaline rocks from west to east may thus represent a continuous series of cumulates crystallising from the bottom upward (Upton, 2013).

Although less well known, the formation of augite syenite from alkali basalt is also illustrated in the 1256.2 ± 1.1 Ma Ulvö gabbro complex (UGC) of the 1.27–1.25 Ga Central Scandinavian Dolerite Group (CSDG) in central Sweden (Hogmalm *et al.*, 2006). The UGC consists of shallow-emplaced saucer-shaped intrusions of alkali olivine basalt, which are 30–100 km in diameter and 100–300 m thick (Buntin *et al.*, 2019; Larson *et al.*, 2008). The Ringkallen alkali gabbro (RAG) of the UGC is a 300-m-thick layered alkali gabbro with preserved bottom and roof contacts. The Sandwich Horizon between the floor and roof series of the RAG contains a differentiated layer, which consists of augite syenite that is made up of hypersolvus alkali feldspar, altered hedenbergite-rich augite clinopyroxene, Fe-Ti oxide, and apatite. Olivine may have been part of the igneous assemblage, but has been completely replaced by secondary minerals. The transition from gabbro cumulate to augite syenite is discrete and may have formed after mobilisation of the interstitial liquid in the floor cumulates (Tillberg, 2012).

The Ilímaussaq alkaline complex comprises (at least) three separate intrusion phases. These are represented by the augite syenite, alkali granite, and agpaitic nepheline syenites. These three rock suites crystallised from separate batches of deep-derived magma, presumably tapping into a common parental magma chamber at depth (Larsen and Sørensen, 1987; Markl *et al.*, 2001). One simple conclusion to draw from this, is that the magma chamber processes involved in producing augite syenite in extreme cases also appear to have the capability to produce agpaitic magma further down the line.

The agpaitic stage of the Ilímaussaq alkaline complex consists of the crystallisation of successively more alkaline igneous rocks. In the roof zone, pulaskite, foyaite, and sodalite foyaite crystallised progressively downwards, which are underlain by a sodalite-rich flotation cumulate called naujaite. From the bottom up, the rhythmically layered so-called kakortokite cumulate was deposited, which consists of rhythmically alternating layers rich in amphibole, eudialyte, and alkali feldspar. The layered

kokortokite sequence transitions into a succession of lujavrite, that sits between the roof and floor series (Larsen and Sørensen, 1987; Upton, 2013; Ussing, 1912). While this rock series is specific to the evolution of the Ilímaussaq alkaline complex and cannot be generalised across all agpaitic rocks, it does provide ample examples of the complex processes that may be involved in the production of highly differentiated agpaitic magmas.

The igneous processes that form agpaitic rocks take place over a large temperature range, from the liquidus of an alkali basaltic or nephelinitic parental magma down to the solidus of lujavrite at 430 °C (Piotrowski and Edgar, 1970; Sood and Edgar, 1970). They also may take place over a large range of different pressures (depths), as suggested by fluid inclusions in sodalite from Ilímaussaq and the results of petrologic modelling of the genesis of the agpaitic Toongi trachyte (Spandler and Morris, 2016).

4.2 Petrogeny and mass balance of the agpaitic rocks in Norra Kärr

Norra Kärr, despite being a relatively small intrusion, contains a rich internal diversity in both mineralogical and geochemical composition as well as complex rock textures and structures. Local town and farm names Gränna, Lakarp, and Kaxtorp therefore decorate the rock names grennaite, lakarpite, and kaxtorpite, accompanied by a rock denominated as pulaskite (Adamson, 1944; Saxon *et al.*, 2015; Törnebohm, 1906). Considering the widespread and convincing evidence for metamorphic overprinting of Norra Kärr (Atanasova *et al.*, 2020, 2017; Blaxland, 1977; Koark, 1969, 1960), deconvolving the detailed igneous and metamorphic signals, which includes renewed igneous processes during partial melting and pegmatoid formation (Sjöqvist *et al.*, 2020), to figure out the constituent rocks' originally igneous states is, in my humble opinion, a precarious endeavour and should be executed carefully with the aid of detailed geochronology to separate apples from oranges.

My approach to study the petrogeny of Norra Kärr has been to work with the (approximated) bulk composition of the intrusion and rock domains. This approach is facilitated by the economic evaluation of Norra Kärr as a mineral resource, which has resulted in a geochemical database with major and trace element data for nearly 10000 drill core samples. The exploration company's predominant sampling strategy consisted of continuous sampling of 2-metre-long sections for the entire intersection of Norra Kärr with breaks at major rock type boundaries. This means that there is a good statistical sample of the bulk of the alkaline rocks, providing representative bulk domain compositions that are less sensitive to magmatic and metamorphic differentiation processes within the complex. Note that the average compositions used here are not NI 43-101 code compliant and should not be mistaken for the composition of the mineral resource (Bowell *et al.*, 2021).

The industrial background also puts some restrictions on the use of the data. Firstly, the rocks are categorised and sampled according to a predetermined scheme of domains based on an ocular inspection, which could lead to inconsistencies between geologists and over time. Secondly, sampling was carried out primarily for economic geological purposes, not for petrology. This means that fine variations and distinctions within a rock domain may, for practical reasons, be baked together into larger rock domains. Examples of this include a transitional zone between KAX and GTM, consisting of alternating “grennaitic” aegirine-rich bands with zirconium and “kaxtorpitic” amphibole-rich bands with titanium in various proportions, resulting in KAG (kaxtorpite with grennaite) and GTK (grennaite with kaxtorpite) subdomains depending on which is most dominant in that section. Similarly, pulaskite occurs both as large bodies and as smaller blocks within a grennaite groundmass. The latter is commonly sampled as a “pulaskite with grennaite” domain (PULG).

Grennaite with pegmatoid veins (PGT) is classified (visually) into seven different subdomains depending on the relative percentages of pegmatoids (5–10, 10–30, 30–50, 50–70, 70–90, >90 %, and a “recrystallised” variety), meaning that the compositional variety of individual pegmatoids is averaged into the bulk composition together with the host grennaite groundmass. Since the pegmatoids occur almost exclusively within the PGT domain, the average bulk PGT composition should be representative of the bulk composition of the entire domain, irrespectively of the relative amounts of pegmatoid and matrix in individual samples.

For the sake of simplification, I have therefore selected the average pulaskite (PUL), average kaxtorpite (KAX), and average PGT grennaite as representatives of rock domains for which I have judged that the effects of sampling, metasomatic exchange between rock domains and to the surrounding granite, and metamorphism have affected their bulk compositions the least. Pulaskite is tentatively regarded as the most primitive and PGT grennaite is the most evolved of the major types of alkaline rock in Norra Kärr, judged by their degree of peralkalinity and concentrations of incompatible elements. The kinship of the rocks in Norra Kärr was also suggested by Adamson (1944). Unfortunately for him, he had no access to analyses of trace elements. Luckily the incompatible element Zr is a major element in Norra Kärr, and, among other factors, it allowed him to define the rock series pulaskite-lakarpite-grennaite on the basis of their increasing content of Zr.

The parental magma for the Norra Kärr alkaline complex is proposed to have been a mantle-derived magma, based on mantle-like isotope signatures of Hf, Nd, and Pb (Kramm and Koark, 1988; Sjöqvist *et al.*, 2020, 2017). In combination with the consistent low anomalies of Eu and Sr relative to other trace elements, which indicate fractional crystallisation of plagioclase, the parental magma composition probably represented an alkali basalt (Atanasova *et al.*, 2020; Sjöqvist *et al.*, 2013). From whole-

The stratigraphic position of kaxtorpites, at the centre of the complex, is not obvious. Its chemical composition suggests that it is a cumulate, which is anomalously enriched in some elements that are depleted in grennaite but not in pulaskite, for example Li, Cs, Zn, and Th (Figure 8). This also implies that the crystallisation of the kaxtorpites cumulate did not precede the formation of pulaskite in Norra Kärr. Kaxtorpites is stratigraphically situated at the top of the layered Norra Kärr intrusion (Atanasova *et al.*, 2017; Saxon *et al.*, 2015) and is intruded by grennaite (Adamson, 1944), but a satisfactory explanation for the occurrence of a pyroxene- and amphibole-rich cumulate above the most evolved grennaite is currently lacking.

Assuming that pulaskite formed from an earlier batch of magma derived from a common parental magma chamber at depth, and, for the sake of simplification, assuming that the PGT grennaite composition is representative of the grennaite magma, some simple inferences can be made about the magma differentiation. By dividing the element concentrations of PGT by PUL, a factor is obtained that represents the relative enrichment or depletion of each individual element. When sorted from largest to smallest, these factors allow the elements to be grouped easily into similarly incompatible and compatible elements (Figure 12). In Ilímaussaq Th, U, La, Cs, Li, Be, and Pb behaved as perfect incompatible elements (Bailey *et al.*, 2001). This cannot be transferred to Norra Kärr, where at least Th, U, Cs, Li, and Be are fractionated by crystallisation of the kaxtorpites cumulate. The most enriched element of the suite of 39 evaluated elements is Pb, which is enriched by a factor 7.92 from the PUL to PGT domain. The absolute concentrations of Pb are, however, low (436 ppm in PGT) and highly depleted relative to other incompatible elements (Figure 8). Other incompatible elements, which are relatively evenly enriched around factor 5.5, are HREE, Zr, Hf, Nb, Ta, and Sn. Highly enriched elements not presented in Figure 12 are for example As, Se, Te, Cd, and Re, which together with the anomalous enrichment of Pb relative to HFSE seems to indicate an enrichment process not solely dependent on fractional crystallisation. Therefore, the enrichment factor of 5.5 is taken as a more modest estimate of the enrichment of incompatible elements due to fractional crystallisation. The relatively stable enrichment of incompatible elements begins to drop off from the LREE in PGT, probably influenced by the relative distribution of LREE and HREE within the different varieties of grennaite (Atanasova *et al.*, 2020, 2017; Saxon *et al.*, 2015; Sjöqvist *et al.*, 2013). The most depleted elements are Th, Ti, Ba, V, Co, and P (factor 0.034).

Assuming that pulaskite, which most likely is not a cumulate, represents a precursor to the grennaite, in the same way that augite syenite is a precursor to lujavrite in Ilímaussaq, and assuming perfect fractionation of HREE, Zr, etc., the PGT grennaite may have formed after an additional 82 % fractional crystallisation of a common magma reservoir at depth after it released the initial pulaskite magma batch. Given that grennaite accounts for approximately 80 % of the known volume of Norra Kärr

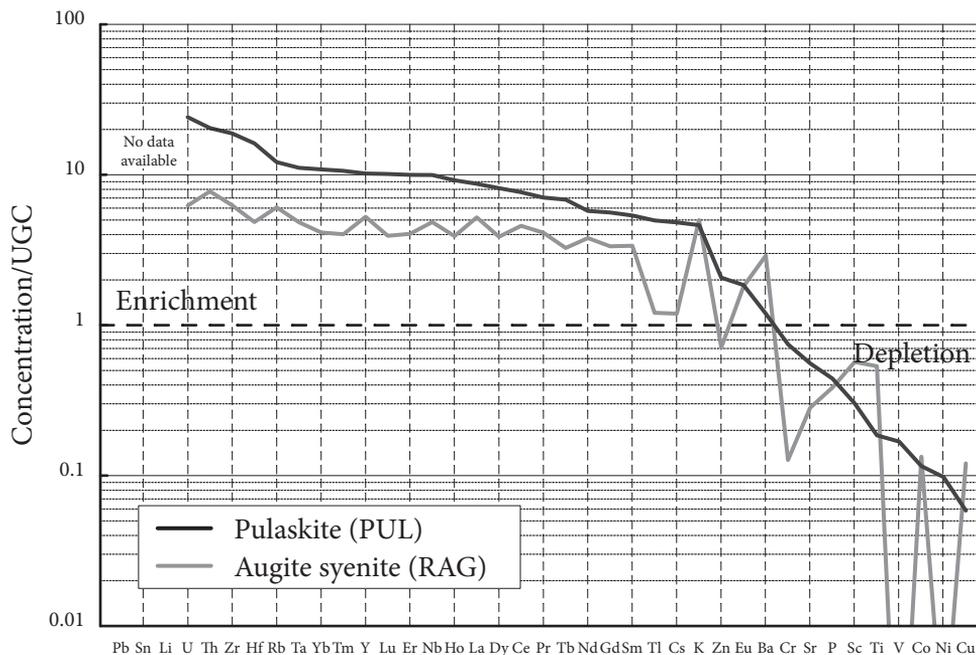


Figure 13. Concentration of trace elements in pulaskite (PUL) and the augite syenite sandwich layer in the Ringkallen alkali gabbro (RAG), normalised against the average chilled margin composition of the Ulvö gabbro complex (UGC) (Larson *et al.*, 2008; Tillberg, 2012).

(Saxon *et al.*, 2015), this implicates that a volume of syenitic cumulate more than 4 times as large as the known volume of Norra Kärr is currently missing from the mass balance of the complex between the formation of pulaskite and grennaite. Although he did not attempt to quantify it, Adamson (1944) also concluded that the pulaskite and lakarpite resembled fragments of rocks that have to be more voluminous constituents than grennaite in a larger unexposed igneous complex.

The grennaite is depleted in Li, Cu, K, Sr, Cr, Ni, Zn, Th, Ti, Ba, V, Co, and P relative to pulaskite (Figure 12). The evolution from pulaskite to grennaite cannot be explained solely by removal of the kaxtorpите cumulate, at least not with the composition of the preserved part of the truncated kaxtorpите body. While elements Li, Cs, Zn, and Th are highly compatible in kaxtorpите and depleted in grennaite relative to pulaskite, fractionation by kaxtorpите crystallisation does not seem to be able to explain the depletion in for instance K, Ba, and P. Therefore, it is likely that pulaskite and grennaite represent sequentially derived magma batches from a common deep-seated parental magma chamber, which evolved by continual fractional crystallisation to explain the majority of grennaite differentiation.

To speculate on the derivation of the pulaskite, it can be normalised against a

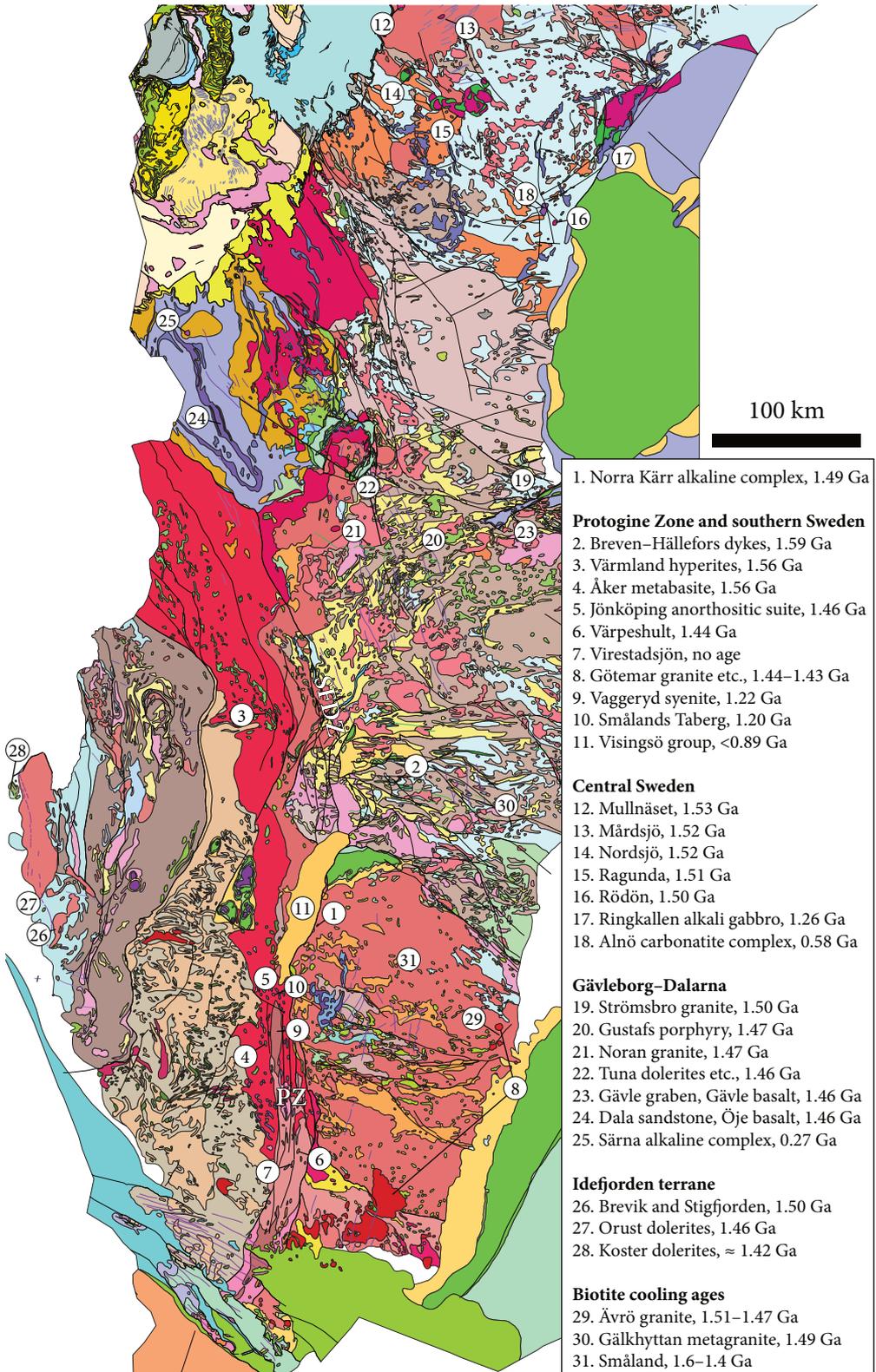
representative alkali basalt, for example the average chilled margin composition of the Ulvö gabbro complex (Larson *et al.*, 2008). If the pulaskite were derived by fractional crystallisation of an alkali basaltic magma with a composition similar to the UGC, it resulted in an enrichment factor of approximately 10 for incompatible elements (Figure 13). This means that the pulaskite could have formed from an alkali basaltic magma after approximately 90 % fractional crystallisation. Combined, this indicates that the grennaite could have formed after 98 % fractional crystallisation of an alkali basaltic magma.

During the fractional crystallisation of the alkali basaltic magma to produce pulaskite, the residual melt was depleted relative to other elements in Zn, Eu, and Ba and depleted in absolute concentrations in Cr, Sr, P, Sc, Ti, V, Co, Ni, and Cu (Figure 13). The depletion of these elements can be explained by the fractional crystallisation of minerals that are common in gabbroic cumulates, comprising olivine (Ni, Co), plagioclase (Eu, Sr), clinopyroxene (Sc), Fe–Ti oxide (Ti, V), apatite (Sr, P), and potentially a sulphide phase (Cu, Ni, Zn). Fractional crystallisation of olivine also depleted the magma in Mg, leading to the low concentrations in pulaskite and especially grennaite. Extensive fractional crystallisation of plagioclase depleted the magma in divalent Eu relative to other REE, causing a low Eu/Eu* ratio. The “plagioclase effect” (Bowen, 1945) also caused the residual magma to become peralkaline, which was further amplified by the crystallisation of alkali feldspar. Given that the Eu/Eu* ratio is similar for both pulaskite (0.40) and grennaite (0.35), fractional crystallisation of plagioclase mainly occurred before pulaskite formation. The high Ge/Si ratio of grennaite ($\approx 8 \times 10^{-6}$) also favours the crystallisation of plagioclase and precludes voluminous crystallisation of garnet, hornblende, and biotite, which would cause a decrease in the Ge/Si ratio of residual magmas due to the high partition coefficient of Ge in these minerals (He *et al.*, 2019).

The late depletion of K, Ba, Th, U, Sr, P, Ti, Li, V, and Co as well as an increase in Rb/K (57 to 104), Na/K mol. (2.1 to 4.7), and decrease in Th/U ratio (3.1 to 0.46) from pulaskite to grennaite seems to indicate the fractional crystallisation of an alkali syenitic cumulate rich in K-rich alkali feldspar (K, Ba, Rb/K, Na/K), Fe–Ti oxide (Ti, V, Co), apatite and/or monazite (P, Sr, Th, U, Th/U), and potentially alkali amphibole (Li).

4.3 Regional geological associations

As stated, one of the main scientific challenges of explaining the origin of the Norra Kärr alkaline complex is the apparent absence of related rocks in the region. The intrusion of the Norra Kärr alkaline complex occurred at 1.49 Ga, determined by U–Pb dating and Hf isotope analysis of zircon by LA-MC-ICP-MS. The zircon formed during syn-magmatic metasomatic alteration (finitisation) of the surrounding



granite (Sjöqvist *et al.*, 2017). The highly differentiated composition of the agpaitic rocks indicates the existence of a larger volume of related syenogabbroic cumulate. In other words, even though Norra Kärr is a relatively small intrusion, it potentially represents a mere 2 % of the total volume of parental magma. Furthermore, from a global point of view, agpaitic rocks are an exceptional occurrence even in alkaline igneous provinces, including the Gardar Province and the Oslo Rift (Neumann *et al.*, 1992; Upton, 2013), which means that most basaltic magmas in alkaline igneous provinces do not differentiate into the agpaitic field. Where are the coeval primitive and intermediate alkaline igneous rocks, related to Norra Kärr?

4.3.1 Mesoproterozoic magmatic and sedimentary rocks in Sweden

Mesoproterozoic rocks in southern Sweden (Figure 14) include the Breven–Hällefors dykes (1.59 Ga) and Värmland hyperites (1.56 Ga) (Söderlund *et al.*, 2005). The Åker metabasite (1.56 Ga) is situated in the Protogine Zone (PZ) south of Lake Vättern (Söderlund and Ask, 2006). Along the PZ, further magmatism includes the emplacement of the Jönköping anorthositic suite (1.46 Ga) and Värpeshult syenogranite (1.44 Ga), and potentially the undated Virestadsjön augite syenite (Brander and Söderlund, 2009; Claesson and Persson, 2019). The southern and south-eastern coasts contain coeval 1.44–1.43 Ga granitoid intrusions, including the Götemar A-type granite (Åhäll, 2001; Sjöqvist and Tillberg, unpublished data). Younger intrusions in the PZ include the Vaggeryd syenite (1.22 Ga) and Smålands Taberg ultramafic intrusion (1.20 Ga) (Larsson and Söderlund, 2005; Söderlund and Ask, 2006).

Approximately 500–600 km north of Norra Kärr, in central Sweden, occurs a suite of bimodal rapakivi complexes. From the Mullnäset intrusion (1.53 Ga), located to the northwest near the Caledonian front, this rapakivi suite displays gradually younger ages toward the southeast, manifested by the Mårdsjö (1.52 Ga), Nordsjö (1.52 Ga), Ragunda (1.51 Ga), and Rödön igneous complexes (Andersson *et al.*, 2002). This region also contains the younger Ringkallen alkali gabbro (1.27 Ga) and the Alnö carbonatite complex (0.58 Ga) (Hogmalm *et al.*, 2006; Meert *et al.*, 2007).

Further south, in the Gävleborg–Dalarna region, three smaller occurrences of rapakivi-related magmatism are known, which show a younging trend to the west. These are the Strömsbro granite (1.50 Ga), NNE- to NE-trending Gustafs porphyry dyke swarm and breccia at Pellesberget (1.47 Ga), and the Noran granite (1.47 Ga) (Andersson, 1997; Claesson and Kresten, 1997; Lundström *et al.*, 2002). The Gustafs porphyry dykes occur over a larger area, including at the Noran granite, where they



Figure 14. Geological map of the Swedish bedrock, 1:1M scale, produced by the Geological Survey of Sweden (SGU), with names and radiometric ages of localities mentioned and cited in the text.

are intimately connected with the abundant NNE- to NE-trending Tuna dolerite dykes (1.46 Ga) (Söderlund *et al.*, 2005). Despite a small radiometric age difference, the magma-mingling field relationships suggest that the dolerite and porphyry dykes are coeval (Hjelmqvist, 1966).

The Gävleborg–Dalarna region also contains preserved Mesoproterozoic sedimentary rocks in the Gävle graben and the Dala sandstone. The youngest concordant zircon in the Dala sandstone implies a maximum deposition age <1.58 Ga. The Strömsbro granite forms part of the basement to the Gävle sandstone. If these sandstones are coeval, then their maximum deposition age could be <1.5 Ga (Lundmark and Lamminen, 2016). Both the Dala and Gävle sandstones contain deposits that have been interpreted as continental flood basalts, the Öje and Gävle basalts, respectively. Age equivalents of the Tuna dolerite dykes (1.46 Ga) have been interpreted as potential feeder dykes to the basalts (Söderlund *et al.*, 2005). The peralkaline Särna alkaline complex (0.27 Ga) lies within a tectonic window in the Dala sandstone (Bylund and Patchett, 1977).

Rocks in the Idefjorden terrane on the Swedish west coast are not discussed here, despite an abundance of Mesoproterozoic rocks. These include the intermingled Brevik gabbro and Stigfjorden granite (1.50 Ga), as well as the N- to NNE-trending Orust dolerite dyke swarm (1.46 Ga), the age of which is reminiscent of the Tuna dolerite dykes (Åhäll and Connelly, 1998). The NNE-trending Koster dolerite dyke swarm (\approx 1.42 Ga, uncertain whole-rock Rb–Sr age) (Hageskov and Pedersen, 1988) broadly lines up with the NNE-trending Tuna dykes and Gävle graben. A discussion about the origin of the juvenile Idefjorden terrane in relation to the rest of the Baltic Shield is beyond the scope of this thesis.

In addition to Mesoproterozoic lithofacies, biotite cooling ages over a large area in south-eastern Sweden are also approximately coeval with the magmatic age of Norra Kärr. These include seven 1.51–1.47 Ga biotite Ar–Ar cooling ages in undeformed Ävrö granite on the east coast, which predate the local Götemar A-type granitic magmatism (Söderlund *et al.*, 2008). Approximately 150 km north, at Gälkhyttan, a single 1.49 biotite Ar–Ar cooling age has been documented (Page *et al.*, 2007).

In 2017, Adi Fazic and I sampled undeformed TIB granites along a >200 km N-S traverse from Gälkhyttan via Finspång to Lessebo for the purpose of regional thermochronology. The polished slabs were evaluated by SEM petrography for signs of alteration of the primary biotite. Ages of unaltered biotite were determined by *in situ* Rb–Sr dating and compared with U–Pb zircon ages from the literature. We could reproduce the 1.49 Ga cooling age at Gälkhyttan (Page *et al.*, 2007). Cooling ages in the traverse from Finspång to Rosenfors in Småland are approximately 1.6–1.4 Ga (Fazic, 2018).

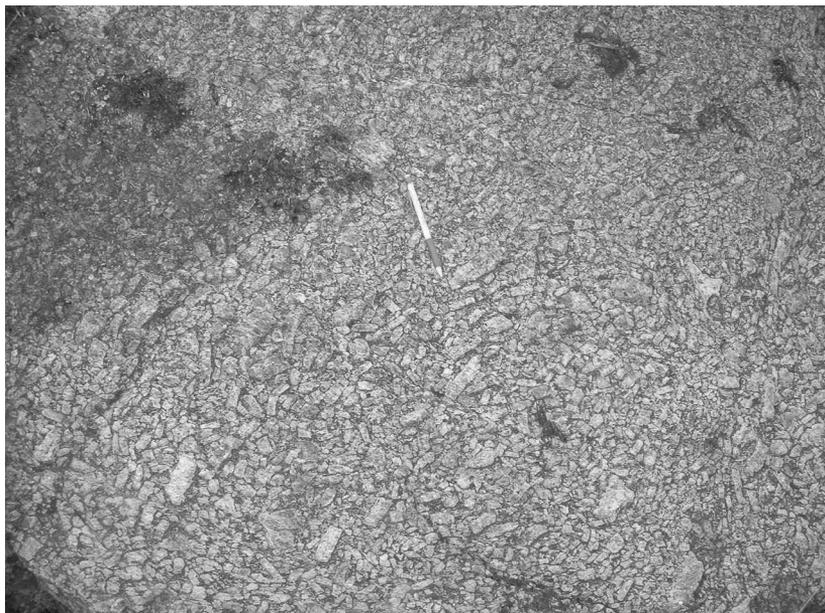


Figure 15. Leuconorite of the Jönköping anorthositic suite (JAS) with abundant plagioclase megacrysts, from the Skinnarebo locality. Photo: Linus Brander.

4.3.2 Connection to the Jönköping anorthositic suite

The location and age of Norra Kärr put it in the larger framework of Mesoproterozoic magmatism along the Protogine Zone. The closest age equivalent rocks in the vicinity of Norra Kärr are members of the 1455 ± 6 Ma (2σ) Jönköping anorthositic suite (JAS), which is a N- to NE-trending collection of plagioclase-porphyritic leuconoritic intrusions with anorthosite rafts up to 5 m across. The plutons typically have dimensions approximately 1 by 0.3 km. They occur in a 25 by 25 km area in the southwestern extension of Lake Vättern, approximately 50 km southwest of Norra Kärr (Brander and Söderlund, 2009; Lundqvist, 1996). The coeval Tuna dolerite dykes, further north, may also carry abundant plagioclase megacrysts although they are not anorthositic (Hjelmqvist, 1966).

The anorthosite component of the JAS resembles Proterozoic massif-type anorthosite (Brander and Söderlund, 2009). The magmatic processes that formed Proterozoic massif-type anorthosites took place over time scales in the order of 100 million years. Geochemistry and geochronology of high-alumina orthopyroxene megacrysts (HAOM) from anorthosites of different ages indicates that these crystallised at high pressure, at or near the crust–mantle boundary, approximately 80–120 million years before the emplacement of the anorthosite massifs in the continental crust (Bybee *et al.*, 2014).

The JAS leuconorite contains abundant plagioclase megacrysts (Figure 15), which at

Table 1. Comparison of major element compositions of rock types from the Särna alkaline complex and catapleiite-porphyritic grennaite (Magnusson, 1923; Sjöqvist *et al.*, 2013).

	Cancrinite tinguaite	Särnaite	Grennaite (GTC)
SiO ₂	51.04	50.83	57.13
TiO ₂	0.29	0.62	0.01
ZrO ₂	—	—	1.58
Al ₂ O ₃	20.47	20.70	19.46
Fe ₂ O ₃ *	4.31	3.23	4.41
MgO	0.97	1.01	0.01
CaO	2.62	4.36	0.55
Na ₂ O	11.62	12.29	11.59
K ₂ O	3.52	2.55	3.63
CO ₂	1.64	1.24	—
H ₂ O	5.85	4.21	—
P ₂ O ₅	0.27	0.31	0.008
LOI	—	—	1.38
Total	102.37	101.14	98.31
Na/K mol.	5.02	7.32	4.85
Agpaitic Index	1.12	1.11	1.18

the Skinnarebo locality contain inclusions of HAOM with Al₂O₃ contents up to 3.6 wt.%. The high Al₂O₃ content in HAOM is caused by crystallisation at high pressure and indicates a polybaric evolution in which the initial crystallisation occurred at greater depth (Brander and Söderlund, 2009).

The HAOM-bearing plagioclase megacrysts indicate its derivation from a deep magma chamber, possibly an underplating basaltic magma at the crust–mantle boundary. The crustal emplacement of the JAS subsequently took place at 1455 ± 6 Ma (2σ) (Brander and Söderlund, 2009). The 30–40-million-year difference in emplacement ages between Norra Kärr and the JAS is well within the limit of reasonable durations of magmatic processes during magma underplating and the formation of massif-type anorthosites (Bybee *et al.*, 2014).

The JAS plagioclase megacrysts and anorthosite rafts probably do not represent the actual cumulate that formed the peralkaline magma of Norra Kärr. However, they provide evidence for a magmatic and tectonic regime at that time, which allowed the ponding of magma at large depth, to cool slowly and crystallise HAOM and large amounts of plagioclase. It is therefore not inconceivable that a similar system existed beneath Norra Kärr, 50 km to the northeast of the JAS, and that fractional

crystallisation of plagioclase and HAOM from a basaltic magma at large depth gave rise to a highly differentiated peralkaline magma.

The predominant N to NE orientation of Mesoproterozoic dolerite and porphyry dykes in Sweden provides an indication of the tectonic stress field in the bedrock at that time. Norra Kärr is located near the eastern side of the Vättern graben. Although the syn-tectonic Visingsö group sediments in the Vättern graben are approximately 600 million years younger than Norra Kärr, the NNE orientation of the graben, in relation to the location of Norra Kärr and the orientation of Mesoproterozoic dykes and JAS, allows speculation into a possible longer development history of the Vättern graben. If the Tonian rifting and sedimentation of the Visingsö group represent the reactivation of an older structure in the crust, the current NNE orientation of the Vättern graben could have been inherited from an earlier phase of extensional tectonic activity around 1.49–1.46 Ga in the Mesoproterozoic Era.

4.4 Comparison to the Särna alkaline complex

Beyond Norra Kärr, another classic locality of peralkaline silica-undersaturated igneous rocks in Sweden is the Särna alkaline complex in Dalarna, which is famous for its primary cancrinite in “särnaite” (peralkaline cancrinite syenite) and the regionally associated tinguaitite dykes (Magnusson, 1923). The characteristic glacial erratics of tinguaitite, which guided Alfred Elis Törnebohm to his discovery of the alkaline complex (Törnebohm, 1883, 1881), have been used to trace ice movement during the last glaciation (Lundqvist, 1997, 1951).

The Särna peralkaline foid syenites and tinguaitites, like Norra Kärr, intruded the TIB, which in Dalarna consists of both volcanic rocks and granite (Lundqvist and Persson, 1999). The age of the Särna rocks is, however, much younger and has been constrained to 287 ± 14 Ma (2σ) by measurements of palaeomagnetism and Rb–Sr dating (Bylund and Patchett, 1977).

At a glance, the whole-rock compositions of the Särna alkaline rocks are similar to grenaite from Norra Kärr (Table 1). They share in common a high concentration of Al_2O_3 and Na_2O , exceptionally high Na/K ratio, and low CaO and Fe_2O_3^* . There are also clear differences, for example the clearly higher TiO_2 , MgO, and P_2O_5 concentrations in Särna, but the initial similarities intrigued me to study the rocks further and evaluate the geochemical similarities and signs of petrogenetic processes.

I made field visits to the Särna area in 2013 and 2017, the latter of which together with John Eliasson. The Särna alkaline complex comprises two steep-flanked hills, but despite this the outcrop exposure is even worse than in Norra Kärr. The hills are

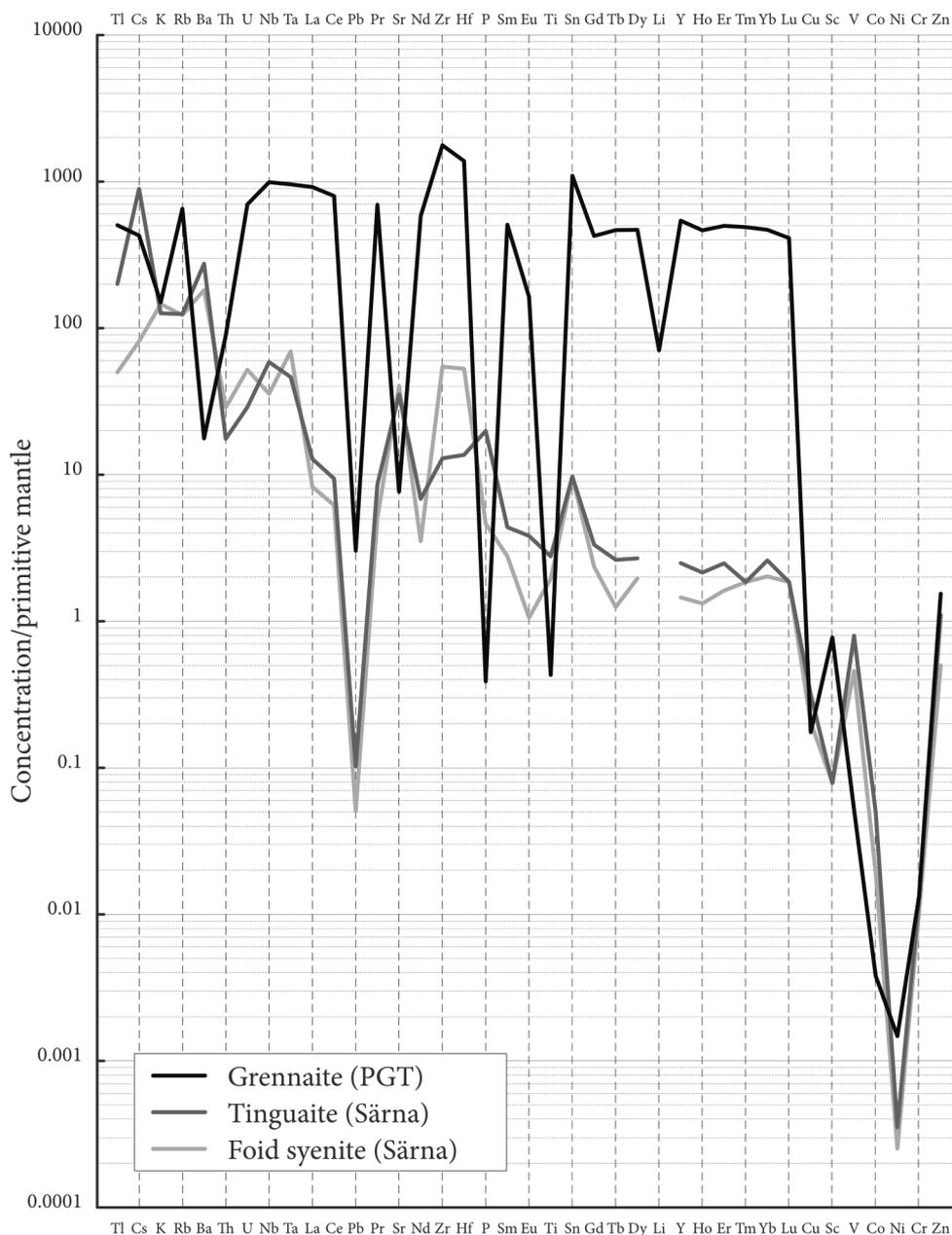


Figure 16. Comparison of trace element concentrations of grennaite (PGT) against tinguaitite and foid syenite from the Särna alkaline complex, normalised against primitive mantle (Lyubetskaya and Korenaga, 2007). The elemental signatures of these two occurrences of peralkaline nepheline syenite in Sweden do not resemble each other, thus excluding a similar origin. Data for Särna was made available by the Geological Survey of Sweden.

largely covered in glacial boulder fields and till as well as a thick layer of moss, leaving only a dozen or so outcrops to be discovered.

Samples of cancrinite syenite and tinguaitite were extensively studied by SEM. Mineral analyses were made by quantitative SEM-EDS analysis. Rare-earth and trace element concentrations of clinopyroxene, cancrinite, and titanite were analysed by LA-ICP-MS. The Särna alkaline rocks are not agpaitic and contain titanite as the primary host for HFSE. The ages of a cancrinite nepheline syenite (294 ± 22 Ma [2σ]) and a biotite-porphyritic tinguaitite dyke (301.9 ± 7.8 Ma [2σ]) were determined by *in situ* Rb–Sr isotope analysis (Hogmalm *et al.*, 2017; Zack and Hogmalm, 2016) of K-feldspar, titanite, cancrinite, and biotite (Eliasson, 2018). This age is coeval with the early stages of the Permian Oslo Rift in southern Norway (Neumann *et al.*, 1992).

Although unsurprising, this is the first geochronological evidence that links the tinguaitite dykes to the Särna alkaline complex, since they were previously undated. Whole-rock Rb–Sr dating of alkaline rocks is notoriously sensitive to disturbance by fluids and crustal contamination (*e.g.* Borst *et al.*, 2019). Together with the dating of alnöite from the Alnö carbonatite complex (Ranjer, 2016), our ages for the särnaite and tinguaitite provide another example of how *in situ* Rb–Sr (and K–Ca) dating (Hogmalm *et al.*, 2017; Kangas, 2018; Sjöqvist *et al.*, 2018; Zack and Hogmalm, 2016), by carefully selecting discrete mineral parageneses and domains suitable for isotope analyses, can be a powerful dating method also for alkaline rocks.

Results from the work of Eliasson (2018) place the Särna miaskitic rocks in stark contrast to Norra Kärr agpaitic rocks, despite both being highly sodic peralkaline foid syenites. The Särna alkaline rocks lack a negative Eu anomaly. They carry low concentrations of HFSE in general and low concentrations of REE in particular, approximately two orders of magnitude below the concentrations found in grennaite. In general, their trace element signatures have little in common (Figure 16).

We can therefore conclude that “swallows are not the only summer birds” (Bowen, 1945, p. 89). There must be multiple geological processes that lead to the formation of highly sodic, peralkaline, alumina-rich, and silica-undersaturated syenitic rocks. One of these gives rise to grennaite, which is highly enriched in incompatible elements, while another gives rise to the särnaite and Särna tinguaitite, which are hardly enriched in incompatible elements and do not involve extensive fractional crystallisation of plagioclase to produce a peralkaline magma.

“

On a small rocky islet in a fiord in southern Norway we stood in the sun, eating raw mussels and marvelling at the prodigious crystals of aegirine in the pegmatite. Later that evening, with the help of some Yugoslavian plum-brandy, we wondered again about the petrologic significance of aegirine and talked of its phase relations.”

—David Kenneth Bailey (1969)

5

Future Research Topics

A BORING PHRASE to use in academia is “more research is needed”. Nonetheless, the geological research completed during the last decade by various working groups leaves plenty of unanswered questions, which may merit further investigation. Here, a few of these are summarised.

- Systematic investigation and classification of the enclosed rocks: pulaskite, lakarpite, kaxtorpite, and other alkaline rocks. The current sampling strategy is generally too crude for detailed petrological work. The enclosed rocks contain mineral assemblages that are transitional between miaskitic and agpaitic rocks and may therefore contribute to an improved general understanding of the stabilisation of agpaitic minerals. Detailed individual sampling of enclaves in the field in addition to systematic sampling in drill cores would aid in understanding their petrological properties and the distribution of the various types enclosed within the grennaite.
- More petrochronology to better constrain the timing of formation of pegmatoid veins in grennaite in relation to local deformation and regional tectonics. Attempts should be made by *in situ* Rb–Sr dating (Hogmalm *et al.*, 2017), although keeping in mind possible effects of thermal resetting and cooling on the

Rb–Sr systematics. Micromill sampling for Sm–Nd ID-TIMS, alternatively by LA-MC-ICP-MS, is a promising geochronological technique in agpaitic rocks (Sjöqvist *et al.*, 2020).

- Detailed investigations to better understand the physicochemical conditions that controlled the suggested formation of partial melts from grennaite during metamorphic overprinting (Sjöqvist *et al.*, 2020). The grennaite domain with pegmatoids plays a central role in the economic assessment of Norra Kärr, and their formation may have been of key importance as an ore-forming process.
- Petrology and geochronology of the centrally located and cross-cutting mafic dykes that intrude Norra Kärr (Saxon *et al.*, 2015), which provide a lower age limit for fabric-forming tectonic processes.
- Research into an economically-viable use for a potential aegirine by-product, which will decrease the on-site waste storage at a hypothetical Norra Kärr mine. According to the 2021 Preliminary Economic Assessment, the bulk rock will be processed into a eudialyte concentrate, a “nepheline syenite” industrial mineral, and an aegirine waste in two stages of magnetic separation (Bowell *et al.*, 2021).

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Appendix I: Abbreviations and units

°C	Degrees centigrade
Agpaitic index	(Na+K)/Al mol.
AI	Alkalinity index: Al-(Na+K) mol.; or Agpaitic index
Al	Aluminium
<i>apfu</i>	Atoms per formula unit
Ar	Argon
As	Arsenic
ASI	Aluminium saturation index: Al/(Ca-1.67P+Na+K) mol.
Ba	Barium
Be	Beryllium
Bi	Bismuth
BSE	Backscattered electron
C	Carbon
Ca	Calcium
Cd	Cadmium
Ce	Cerium
CIPW	Cross, Iddings, Pirsson, Washington; Cross <i>et al.</i> , 1902
Cl	Chlorine
Cr	Chromium
Co	Cobalt
CRM	Critical raw material
Cs	Caesium
CSDG	Central Scandinavian Dolerite Group
Cu	Copper
Dy	Dysprosium
ϵ_{Nd}	$(\{[^{143}Nd/^{144}Nd]X(t)/[^{143}Nd/^{144}Nd]CHUR(t)\} - 1) \times 10000$
ϵ_{Hf}	$(\{[^{176}Hf/^{177}Hf]X(t)/[^{176}Hf/^{177}Hf]CHUR(t)\} - 1) \times 10000$
EC	European Commission
EDS	Energy dispersive spectrometry
EGM	Eudialyte-group minerals, eudialyte <i>sensu lato</i>
EMP	Electron micro-probe
Er	Erbium
ERECON	European Rare Earths Competency Network
EU	European Union
Eu	Europium
Eu/Eu*	$Eu_N / (Sm_N \times Gd_N)^{0.5}$
F	Fluorine
Fe	Iron
Ga	Gallium
Ga	Billion years ago

Ge	Germanium
ID-TIMS	Isotope dilution thermal ionisation mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
In	Indium
JAS	Jönköping anorthositic suite
H	Hydrogen
HAOM	High-alumina orthopyroxene megacryst
Hf	Hafnium
HFSE	High-field-strength elements: <i>e.g.</i> Zr, Ti, Nb, REE
IAC	Ion-adsorption clay
K	Potassium
km	Kilometre
km ³	Cubic kilometre
La	Lanthanum
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
LA-MC-ICP-MS	Laser ablation multi-collector inductively coupled plasma mass spectrometry
Li	Lithium
LILE	Large-ion-lithophile elements
LREE	Light rare-earth elements: La, Ce, Pr, Nd, Pm, Sm
LREO	Light rare-earth oxide
Lu	Lutetium
Gd	Gadolinium
Hf	Hafnium
Ho	Holmium
HREE	Heavy rare-earth elements: Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
HREO	Heavy rare-earth oxide
m	Metre
Ma	Million years ago
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
mol.	Molecular, molar
Mt	Million tonnes
N	Nitrogen
Na	Sodium
Nb	Niobium
Nd	Neodymium
Ni	Nickel
O	Oxygen

P	Phosphorous
Pb	Lead
Pm	Promethium
ppm	Parts per million
Pr	Praseodymium
PZ	Protogine Zone
QA/QC	Quality assurance/quality control
RAG	Ringkallen alkali gabbro
Rb	Rubidium
Re	Rhenium
REE	Rare-earth elements; Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
S	Sulphur
Sc	Scandium
Se	Selenium
SEM	Scanning electron microscope
SFDZ	Sveconorwegian Frontal Deformation Zone
Si	Silicon
Sm	Samarium
Sn	Tin
Sr	Strontium
Ta	Tantalum
Tb	Terbium
Te	Tellurium
Th	Thorium
Ti	Titanium
TIB	Transscandinavian Igneous Belt
Tl	Thallium
TL	Type locality
Tm	Thulium
TREO	Total rare-earth oxide
U	Uranium
UGC	Ulvö gabbro complex
V	Vanadium
W	Tungsten
WDS	Wavelength dispersive spectrometry
Wt. %	Weight percent
Y	Yttrium
Yb	Ytterbium
Zn	Zinc
Zr	Zirconium

Appendix II: Definitions

Acmite	See: Aegirine
Aegirine	$\text{NaFe}^{3+}\text{Si}_2\text{O}_6$
Aegirine lujavrite	Lujavrite with aegirine
Aegirine-augite	$(\text{Na}, \text{Ca}, \text{Fe}^{2+}, \text{Mg})(\text{Fe}^{3+}, \text{Al}, \text{Fe}^{2+}, \text{Mg})\text{Si}_2\text{O}_6$
Agpaitic rock	Rock with complex Na-HFSE minerals, cf. Miaskitic
Albite	$\text{NaAlSi}_3\text{O}_8$
Alkali basalt	Chemically-defined basalt with normative nepheline
Alkali feldspar	$(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$
Alkali granite	Peralkaline granite with alkali amphibole or pyroxene
Alnöite	Rock with phenocrysts of phlogopite, olivine, and augite in a groundmass with melilite, augite, and biotite
Amphibole	Supergroup; $\text{AB}_2\text{C}_5((\text{Si}, \text{Al}, \text{Ti})_8\text{O}_{22})(\text{OH}, \text{F}, \text{Cl}, \text{O})_2$
Andalusite	Al_2SiO_5
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Anorthosite	Rock consisting of >90 % plagioclase
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})$
Arfvedsonite	$\text{NaNa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$
Augite	$(\text{Ca}, \text{Mg}, \text{Fe})(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$
Augite syenite	Syenite with augite
Autolith	Inclusion of a genetically-related rock
Baddeleyite	ZrO_2
Biotite	$\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
Britholite group	$(\text{REE}, \text{Ca})_5((\text{Si}, \text{P})\text{O}_4)_3\text{X}$
Cancrinite	$(\text{Na}, \text{Ca}, \square)_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{CO}_3, \text{SO}_4)_2 \cdot \text{H}_2\text{O}$
Carbonatite	Igneous rock with >50 % modal carbonate minerals
Catapleiite	$\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$
Chondrite	CI chondrite, meteorite similar in composition to the Sun
Clinopyroxene	ABSi_2O_6
Cordierite	$(\text{Mg}, \text{Fe})_2\text{Al}_3(\text{AlSi}_5\text{O}_{18})$
Cumulate	Igneous rock formed by accumulation of crystals
Diopside	$\text{CaMgSi}_2\text{O}_6$
Dolerite	Rock of intermediate grain size between basalt and gabbro consisting mainly of plagioclase and pyroxene
Eckermannite	$\text{NaNa}_2(\text{Mg}_4\text{Al})\text{Si}_8\text{O}_{22}(\text{OH})_2$
Eudialyte	$\text{Na}_{15}\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{73})(\text{O}, \text{OH}, \text{H}_2\text{O})_3(\text{Cl}, \text{OH})_2$
Fe-Ti oxide	See: Ulvöspinel; Ilmenite; Titanomagnetite
Feldspar	$(\text{K}, \text{Na}, \text{Ca})\text{Al}(\text{Si}, \text{Al})_3\text{O}_8$
Feldspathoid	Silica-poor feldspathic minerals, never occur with quartz, include cancrinite, leucite, nepheline, and sodalite
Fenite	Metasomatic rock associated with alkaline rocks, rich in

	alkali feldspar and alkali pyroxene and/or amphibole
Ferro-syenogabbro	Iron-rich rock intermediate between gabbro and syenite
Fluoroleakeite	$\text{NaNa}_2(\text{Mg}_2\text{Al}_2\text{Li})(\text{Si}_8\text{O}_{22})\text{F}_2$
Foid	See: Feldspathoid
Foyaite	Hypersolvus nepheline syenite with platy alkali feldspar
Fractional crystallisation	Removal of mineral precipitates from a melt
Gabbro	Rock consisting mainly of plagioclase and clinopyroxene
Garnet group	$\text{X}_3\text{Z}_2(\text{SiO}_4)_3$
Granite	Rock consisting of quartz, plagioclase, and alkali feldspar
Grennaite	Agpaitic nepheline syenite aegirine, nepheline, albite, microcline, eudialyte, and commonly catapleiite
Hawaiite	Na-rich variety of trachybasalt
Hedenbergite	$\text{CaFeSi}_2\text{O}_6$
Hornblende	$\square\text{Ca}_2((\text{Mg},\text{Fe})_4\text{Al})(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$
Hyperagpaitic	Extremely peralkaline rock with <i>e.g.</i> naujakasite, zirsinalite, ussingite, and others
Ilmenite	FeTiO_3
Jadeite	$\text{NaAlSi}_2\text{O}_6$
Kakortokite	Layered agpaitic nepheline syenite with layers enriched in alkali feldspar, eudialyte, and arfvedsonite
Kaxtorpite	Peralkaline nepheline syenite with alkali feldspar, nepheline, and fluoroleakeite sometimes with pectolite and/or aegirine
Lakarpite	Agpaitic nepheline syenite with albite, nepheline, alkali amphibole, and minor microcline with rinkite- and/or eudialyte-group minerals
Leucite	KAlSi_2O_6
Lopolith	Lenticular igneous intrusion, depressed central region
Lorenzenite	$\text{Na}_2\text{Ti}_2(\text{Si}_2\text{O}_6)_3\text{O}_3$
Lujavrite	Agpaitic nepheline syenite with eudialyte, arfvedsonite and/or aegirine, nepheline, and alkali feldspar
Melilitite	Volcanic rock consisting mainly of melilite and pyroxene
Miaskitic rock	Rock with zircon and titanite hosting HFSE, cf. Agpaitic
Mica	Family of sheet silicates, including muscovite and biotite
Microcline	KAlSi_3O_8
Migmatite	Metamorphic rock consisting of lighter and darker parts, segregated by partial melting or differentiation
Monazite	$\text{REE}(\text{PO}_4)$
Mosandrite-(Ce)	$(\text{Ca}_3\text{REE})((\text{H}_2\text{O})_2\text{Ca}_{0.5}\square_{0.5})\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OH})_2(\text{H}_2\text{O})_2$
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
Natrolite subgroup	Subgroup of the zeolite-group minerals
Naujaite	Nepheline sodalite syenite, poikilitic sodalite enclosed in

	alkali feldspar, arfvedsonite, aegirine, and eudialyte
Naujakasite	$(\text{Na},\text{K})_6(\text{Fe}^{2+},\text{Mn}^{2+},\text{Ca})(\text{Al},\text{Fe})_4\text{Si}_8\text{O}_{26}$
Naujakasite lujavrite	Hyperagpaitic arfvedsonite lujavrite with naujakasite
Nepheline	$\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$
Nepheline syenite	Rock consisting mainly of nepheline and alkali feldspar
Nephelinite	Rock consisting mainly of nepheline and clinopyroxene
Ocean island basalt	Variety of intraplate basalt
Olivine	$(\text{Mg},\text{Fe})_2\text{SiO}_4$
Orthopyroxene	$(\text{Mg},\text{Fe})\text{SiO}_3$
Pectolite	$\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$
Pegmatite	Coarse-grained igneous rock
Pegmatoid	Silica-undersaturated pegmatite
Perovskite	CaTiO_3
Phlogopite	$\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
Plagioclase	$(\text{Ca},\text{Na})\text{Al}(\text{Si},\text{Al})_3\text{O}_8$
Pulaskite	Nepheline-bearing alkali syenite with alkali feldspar, sodic pyroxene and/or amphibole, and minor nepheline
Quartz	SiO_2
Riebeckite	$\square\text{Na}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$
Rinkite-(Ce)	$(\text{Ca}_3\text{Ce})\text{Na}(\text{NaCa})\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$
Särnaite	Cancrinite nepheline syenite
Sodalite	$\text{Na}_4(\text{Al}_3\text{Si}_3)\text{O}_{12}\text{Cl}$
Sodalite foyaite	Foyaite with sodalite
Sodalite syenite	Syenite with sodalite
Sodium metasilicate	Na_2SiO_3
Spinel	MgAl_2O_4
Steenstrupine-(Ce)	$\text{Na}_{14}\text{Mn}^{2+}_2\text{Fe}^{3+}_2\text{Ce}_6\text{Zr}(\text{Si}_6\text{O}_{18})_2(\text{PO}_4)_6(\text{PO}_3\text{OH})(\text{OH})_2$
Syenite	Rock consisting mainly of alkali feldspar
Tinguaite	Variety of alkaline volcanic rock with alkali feldspar, aegirine, nepheline with or without other foids, and interstitial aegirine needles (tinguaitic texture)
Titanomagnetite	$\text{Fe}^{2+}(\text{Fe}^{3+},\text{Ti})_2\text{O}_4$
Titanite	$\text{CaTi}(\text{SiO}_4)\text{O}$
Trachyte	Volcanic rock composed mainly of alkali feldspar
TREO	Total rare-earth oxide
Ulvöspinel	TiFe_2O_4
Ussingite	$\text{Na}_2\text{AlSi}_3\text{O}_8\text{OH}$
Villiaumite	NaF
Willemite	ZnSiO_4
Xenocryst	Inclusion of crystal from a foreign rock
Xenolith	Inclusion of a foreign rock
Zircon	ZrSiO_4

Appendix III: Norra Kärr rock domain codes

Domain	Code	Short description
GTC	GTC	Grennaite, catapleiite-porphyritic
	GTCE	Grennaite, catapleiite- and eudialyte-porphyritic
	GTMC	Grennaite, catapleiite-porphyritic, recrystallised
	GT	Grennaite, fine-grained, sometimes with thin platy catapleiite
PGT	GT1	Grennaite with 5–10 % pegmatoids
	GT2	Grennaite with 10–30 % pegmatoids
	GT3	Grennaite with 30–50 % pegmatoids
	GTP	Grennaite with 50–70 % pegmatoids
	PGT	Grennaite with 70–90 % pegmatoids
	NEP	Nepheline syenite pegmatoid, >90 %
	GTR	Grennaite, medium-grained, foliated, “recrystallised”
GTM	GTM	Grennaite, “migmatitic”
	GTMi	Grennaite, incipient “migmatitic”
PUL	PUL	Pulaskite
	PULF	Pulaskite or fenitised granitoid
	PULG	Pulaskite in grennaite
KAX	KAX	Kaxtorpite
	KAG	Kaxtorpite with grennaite bands
	GTK	Grennaite with kaxtorpite bands
LAK	LAK	Lakarpite
	LAKM	Lakarpite, mafic
	ELAK	Lakarpite, eudialyte-bearing
	AUN	Alkaline rock, unspecified
	MAF	Mafic dyke
	MAFJ	Mafic dyke, N-S trending centrally located in Norra Kärr syncline
	MAA	Mafic rock, alkali-rich
	MHYB	Mafic rock, same as MAA, with hydrothermal alkaline minerals
	DOL	Dolerite, eastern
	FEN	Fenite
	MYL	Mylonite
	PEG	Granitic pegmatite
	GR	Granitoid
	SYE	Syenite
	SYP	Syenite pegmatite