DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2016/20

Report of the activities in the ruby project 2014

Nynke Keulen, Majken D. Poulsen & Rita Salimi

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
DANISH MINISTRY OF ENERGY, UTILITIES AND CLIMATE

GEUS

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G E U S

Contents

1. Executive Summary

This project on the evaluation of Greenlandic rubies is part of a collaboration project between the Ministry of Mineral Resources in Nuuk, Greenland, and the Geological Survey of Denmark and Greenland, Copenhagen & Nuuk, Denmark. The investigations are mainly focused on characterisation of the Fiskenæsset complex ruby/sapphire, because a mine is currently being built in the most promising ruby outcrop in that area, Aappaluttoq, by the Canadian company True North Gems (TNG).

The activities in 2014 consist of multivariate statistics analyses of the geochemical results for the ruby/sapphire samples that were collected in 2011-2013 (Chapter 2). We show that Aappaluttoq samples, especially the samples with an intensive red colour, have a rather unique geochemical signature, or 'fingerprint', but still have a close resemblance to some international mafic-ultramafic occurrences.

Mineral inclusions and other internal growth features were studied with an optical stereo microscope. Anthophyllite and phlogopite are common mineral inclusions in samples from the Fiskenæsset complex, while milky zones, zonal clouds form typical internal features. A range of features, including trace element geochemistry, oxygen isotope values and internal features, needs to be investigated to be able –in some cases- to separate samples from Fiskenæsset from other international occurrences.

The project included some travelling activity in 2014, both for educational (Dubai, Chapter 4) and for dissemination purposes (GIT conference in Thailand, where an abstract was presented on the comparison of geochemical methods for fingerprinting of Greenlandic gem-corundum (ruby/sapphire)). The abstract and poster for the GIT conference are added as Appendix.

The samples from the Fiskenæsset area contain both ruby (reddish colours) and sapphire in various shades of pink. Only transparent medium light to dark tones of red to purple red coloured corundum can be defined as ruby. Stones that have light to medium light tone are called pink sapphire. Not all the stones investigated are of gem-quality, and therefore the word for corundum will be used for both ruby and pink sapphire in the following text, unless the actual colours of the ruby/sapphire are described. Even here will ruby or sapphire describe a specific colour of corundum of gem or none-gem quality.

2. Multivariate statistics investigations

2.1 Methods and samples

In this report we apply a multivariate statistical approach to determine the provenance of ruby/sapphire, and particularly to test whether the occurrences of the Fiskenæsset region in southern West Greenland are distinct compared to other global ruby/sapphire occurrences.

2.1.1 Principle component analysis

Multivariate statistical analysis is an often applied technique for examining relationships among multiple variables at the same time. This type of analysis is, among others, used in studies that involve more than one independent variable and can in this way be used as a prediction tool. The provenance of ruby/sapphire can be defined by a range of features, like characteristic trace element distribution, oxygen isotope signature, or distinct inclusions of minerals or fluids, or by distinctive peaks in a spectrum obtained with spectrometry. Ideally each feature will give a range of possible provenance areas, while a combination of several features (principally, as many as possible) will restrict the number of possible areas. In the most ideal case the area of origin of the ruby/sapphire can be fingerprinted by a combination of independent techniques.

For this multivariate statistics study on the Greenlandic ruby and pink sapphire, a principal component analysis (PCA) has been performed. For the analysis the software SiroSOM, developed by CSIRO, Australia, has been applied. PCA is an often-applied technique for visualizing high dimensional data. PCA reduces the dimensionality (the number of variables) of a dataset by maintaining as much variance as possible. This is done by rotating the original data space such that the axes of the new coordinate system point into the directions of highest variance of the data. These axes of variance are termed principal components (PCs) and are ordered by degree of variance: The first component, PC1, represents the direction of the highest variance of the data. The direction of the second component, PC2, represents the highest of the remaining variance orthogonal to the first component (e.g. Scholz, 2006).

SOM in SiroSOM stands for Self Organising Maps. This is a visualisation tool for PCA. The software defines clusters of samples with a high similarity when all variables are taken in account. These are then plotted near each other on a map of all samples. The maps are wrapping around horizontally and vertically; this means that samples in the upper left and upper right corner are very similar; just like samples from the top left and bottom left part of the map.

2.1.2 Samples and applied data sets

For this multivariate statistics study the results for 70 ruby and pink sapphire samples have been used. From this set, 50 samples have been analysed at GEUS for their trace element composition, of these 36 samples from Greenland and 14 samples from other countries. Furthermore, trace element geochemistry data from 20 samples described in literature have been used to supplement the data set with more international occurrences (Calligaro, 1999; Calvo del Castillo, 2009; Pornwilard, 2011; Rakontondrazafy, 2008; Schwarz, 2008; Keulen et al., unpublished data). Data for Mg, Si, Ti, V, Cr, Fe and Ga have been applied in this multivariate study; these elements occur in significant quantities in ruby/sapphire and are traditionally found to be good indicators of provenance.

The trace element geochemistry data has been supplemented with data for oxygen isotopes from the following three studies: The Greenlandic data originates from Kalvig & Keulen (2011), while most of the international data is taken from Giuliani et al. (2005), supplemented with newer data for Madagascar (Giuliani et al. 2007) and Tanzania (Keulen et al., unpublished).

Because nearly none of the samples were analysed for trace element geochemistry and oxygen isotopes in the same study, the matching between oxygen isotope data and geochemistry data is not necessarily optimal. For example for all the Aappaluttoq samples, the same oxygen isotope value $\delta_{18}O$ =4.20‰ has been applied, as this is the only value available to us. In cases where more than one oxygen isotope value was available, the average of the analyses on the ruby/sapphire has been applied. Despite these disadvantages that come with the stable oxygen isotope data, we find it useful to include this independent dataset.

2.2 Results for ruby/sapphire samples

The results for the Self Organising Maps (SOM; Kohonen 2001) and cluster analysis of all investigated samples are shown in Figure 1. Warm colours indicate a high amount of clustering. The results for all samples (Fig. 1A) are compared with the SOMs for Aappaluttoq (Fig. 1B) and for Chromium (Fig. 1C). The clustering based on all samples is shown in the cluster map (Fig. 1D). The four maps show that the samples from Aappaluttoq, Upper Annertussaq, and Rubin Ø together form the light blue cluster (Fig. 1D) and this cluster is strongly influenced by the Cr-concentration of the samples (Fig. 1C). Samples from the other Fiskenæsset outcrops mainly plot in the adjacent brown, purple, dark yellow, dark blue and orange cluster, together with a number of international occurrences.

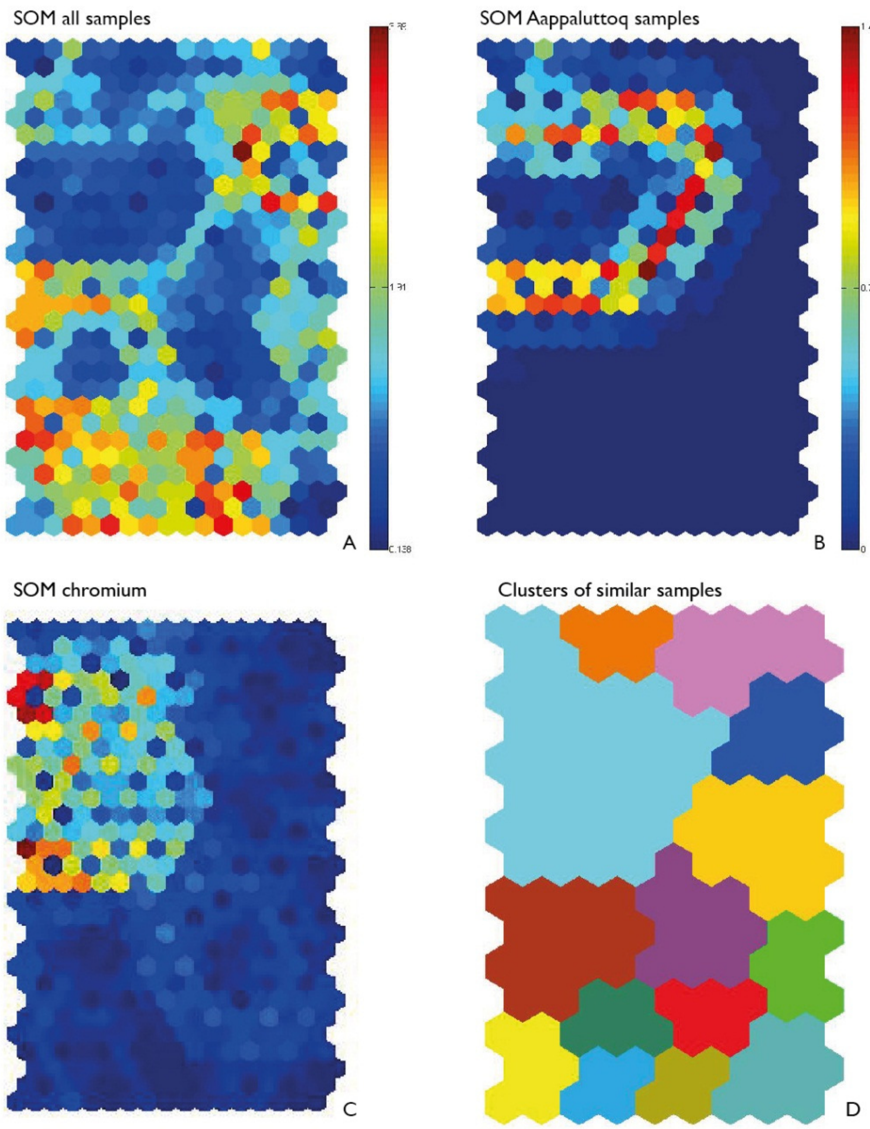


Figure 1. *Self Organising Maps for all (A) analysed samples and (B) for all Aappaluttoq samples, taking in account their trace elements Mg, Si, Ti, V, Cr, Fe, Ga concentrations and δ18O values, (C) SOM for Chromium concentration, and (D) cluster analyses in which similar samples are grouped into one cluster. Aappaluttoq, Rubin Ø, and Upper Annertussaq samples are grouped in the light blue cluster.*

Figure 2 shows the variation in the data between the Aappaluttoq samples and the other samples. The R^2-value is indicated, which is a statistical measure of how well the data fit to the modelled average data. The samples from Aappaluttoq plot in three different R^2-value levels. The samples from Aappaluttoq that are the most typical for Aappaluttoq and the least similar to samples from other areas are 521101, 521105, 521106, 521107, 521110, and 521113 (Fig. 2; sample numbers in Table 1). Samples 521108, 521109 and 521121 form a second group of Aappaluttoq samples, with many similarities to the previous samples, but also to the samples from Upper Annertussaq. Samples 521104, 521111 and 521120 from Aappaluttoq resemble the sample from Rubin Ø.

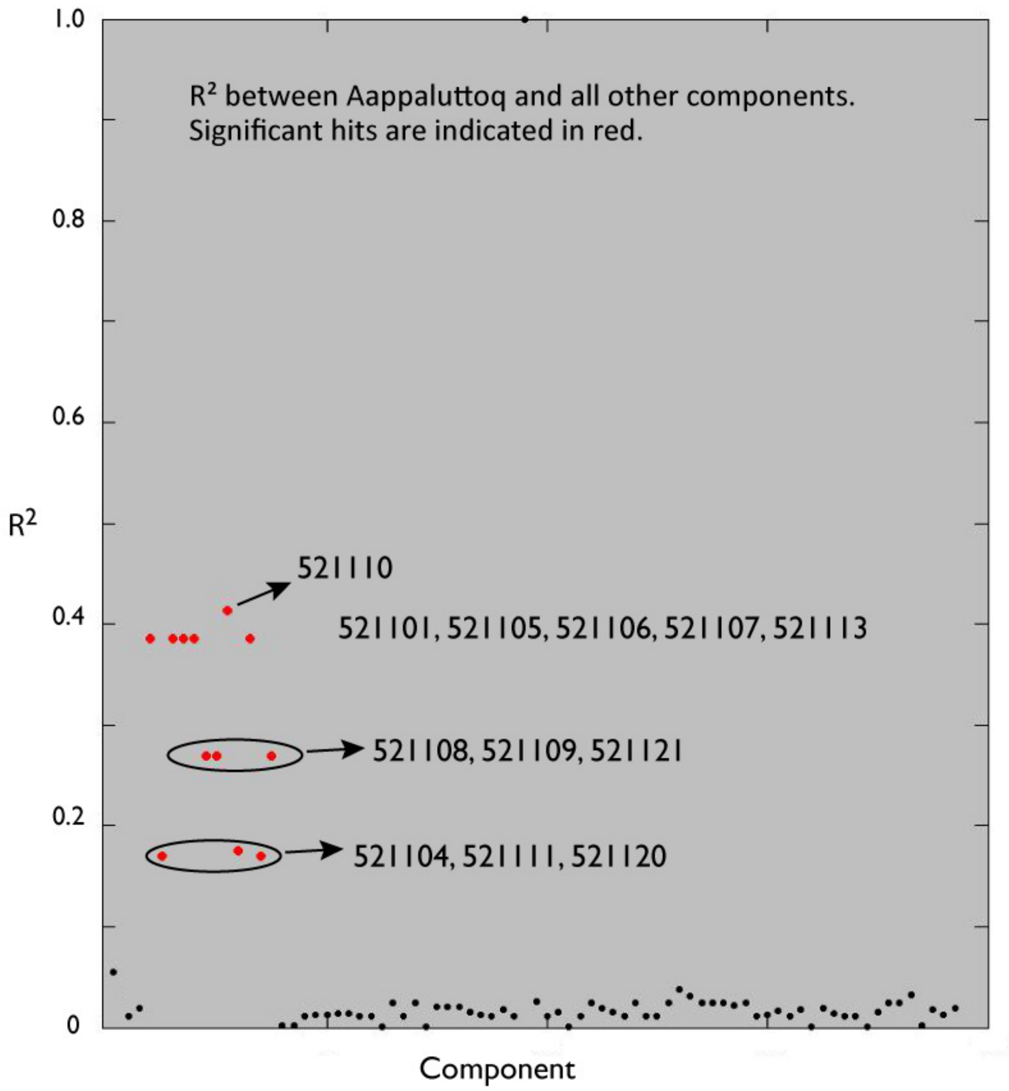


Figure 2. *R^2-values for a component correlation (horizontal axis) between Aappaluttoq and other investigated components. All indicated sample numbers are from Aappaluttoq samples. Significant hits have an R^2 value larger than 0.16.*

Figure 3 shows the principle component analysis for the two main principal components (PC1 vs PC2). The positions of the individual points in the Figure are defined by

the software. The analysed variable Fe, Cr, Ti, V, Ga, Si, Mg and $\delta^{18}O$ values are plotted in the Figure together with the average results for the individual areas. Variables that plot far away from the origin are important for separation of the individual components (e.g. Fe, $\delta^{18}O$ or Si), while variables closer to the origin (like Mg) are relatively unimportant to separate individual areas. Variables that plot in the same quadrant correlate with the individual area (Aappaluttoq has a high Fe, Cr, and Si concentration compared to other areas), variables that plot in opposite quadrants anticorrelate (Aappaluttoq has very low $\delta^{18}O$ values). Individual areas that show up close to Aappaluttoq in the PCA diagram (Fig. 3) are similar in fingerprint to Aappaluttoq.
The cluster analysis and PCA show that the Aappaluttoq samples as a singular group resemble the samples from other parts of the Fiskenæsset complex, most notably Kangarssuk, Qororssuaq, Upper Annertussaq, Rubin Ø, and the samples from international occurrences in Longido (Tanzania), Winza (Tanzania), Chanthaburi (Thailand), Ilalaka (Madagascar), Bo Rai (Thailand), Pailin (Cambodia), Andilamena (Madagascar) and Umba (Tanzania). All show geochemical signatures that overlap or closely resemble the samples from the Fiskenæsset complex and those that have oxygen isotope data generally show low values, like the Fiskenæsset complex (compare to Figure 4).

Table 1: Investigated samples from the Fiskenæsset complex

sample #	Outcrop	sample #	Outcrop
521101	Aappaluttoq	459905	Sarfaq
521104	Aappaluttoq	459991	Kangarssuk
521105	Aappaluttoq	476373	Tuk
521106	Aappaluttoq	497386	Top 670
521107	Aappaluttoq	508660	Qaqqatsiaq
521108	Aappaluttoq	521123	U. Annertussaq
521109	Aappaluttoq	521127	U. Annertussaq
521110	Aappaluttoq	521130	L. Annertussaq
521111	Aappaluttoq	521131	Bjørnesund 2008
521111	Aappaluttoq	521132	Bjørnesund 2008
521113	Aappaluttoq	521134	Bjørnesund 2008
521120	Aappaluttoq	521135	Bjørnesund 2008
521121	Aappaluttoq	521138	Siggartartulik
160063	Qaqqatsiaq	521140	Siggartartulik
510132	Qororssuaq East	521142	Rubin Ø
160098	Beer Mountain	521149	Kigutilik
497391	Beer Mountain	521163	Intex

For the Aappaluttoq samples, typical Mg-concentrations are 40 ppm, Si ≈ 1000 ppm, Ti ≈ 80 ppm, V ≈ 60 ppm, Cr >4000 ppm, Fe ≈ 2500 ppm, Ga ≈ 30 ppm, and $\delta^{18}O$ ≈ $4‰_{(SMOW)}$. Of these values, Cr and Fe have the highest significance, while Ti, Ga, V and $\delta^{18}O$ values can be used in combination to separate Aappaluttoq from other occurrences.

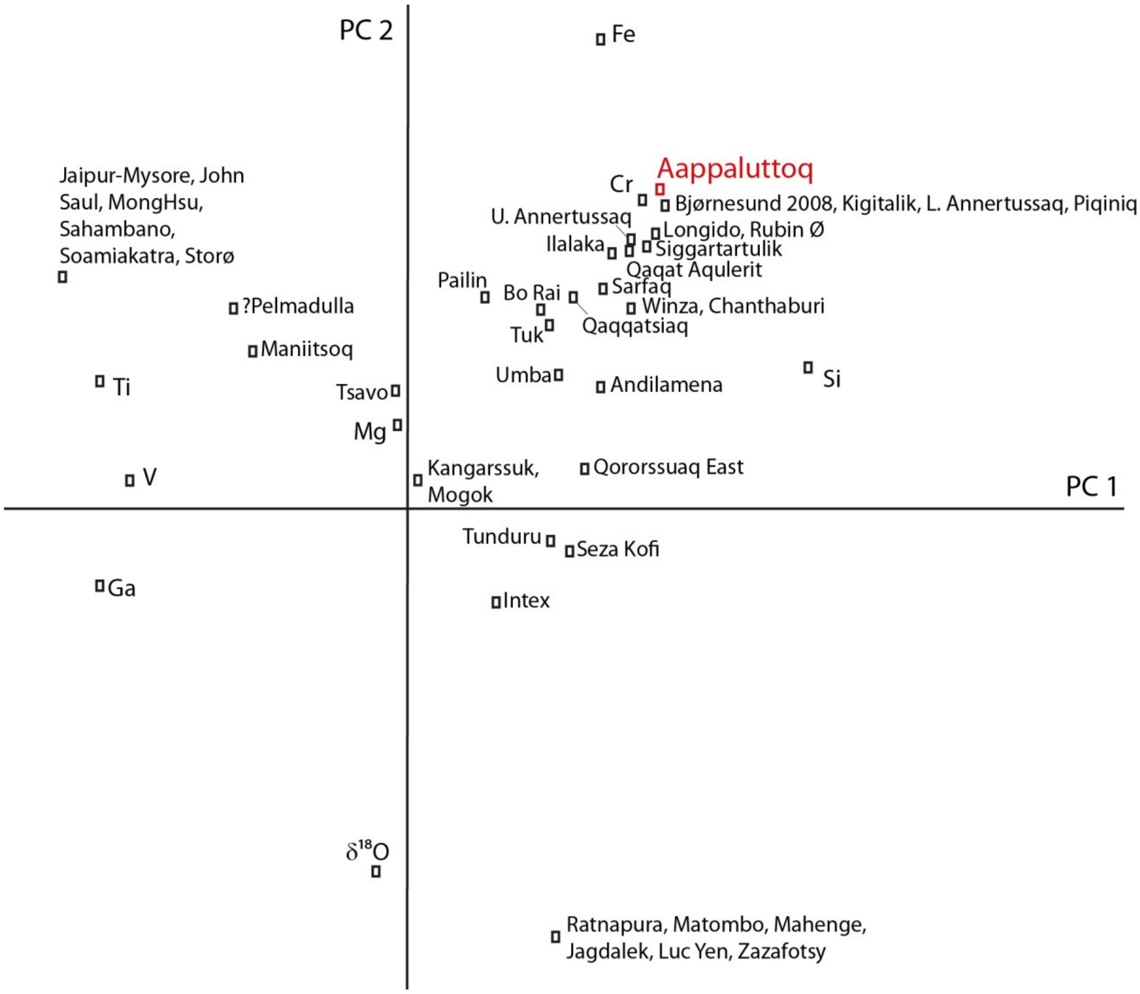


Figure 3. *Principle component analysis (PC1 vs PC2) for the trace element and stable oxygen isotope compositions from all investigated regions. The PCA is based on a dataset including Mg, Si, Ti, V, Fe, Cr, Ga and $\delta^{18}O$.*

2.3 Discussion and summary of the multivariate statistics investigations

The discussion on the applicability of oxygen isotopes and trace element geochemistry for fingerprinting is given in Keulen & Poulsen (2014) and will not be repeated here.

Samples 521101, 521105, 521106, and 521110 are the four samples mentioned in Keulen & Kalvig (2013) as the four most transparent and most intensively red-coloured samples from Aappaluttoq in the Fiskenæsset complex. Samples 521107 and 521113 were analysed subsequently in 2014, and especially sample 521107 is characterised by high chromium values (Keulen & Poulsen, 2014). Therefore, it would seem that the samples that are most significant and typical for Aappaluttoq (Fig. 2) are also the samples with the highest quality, and the samples that are most distinct from corundum from other localities. This fact will help in the fingerprinting of Aappaluttoq samples, as it shows that the high quality samples from Aappaluttoq have a specific geochemical signature.

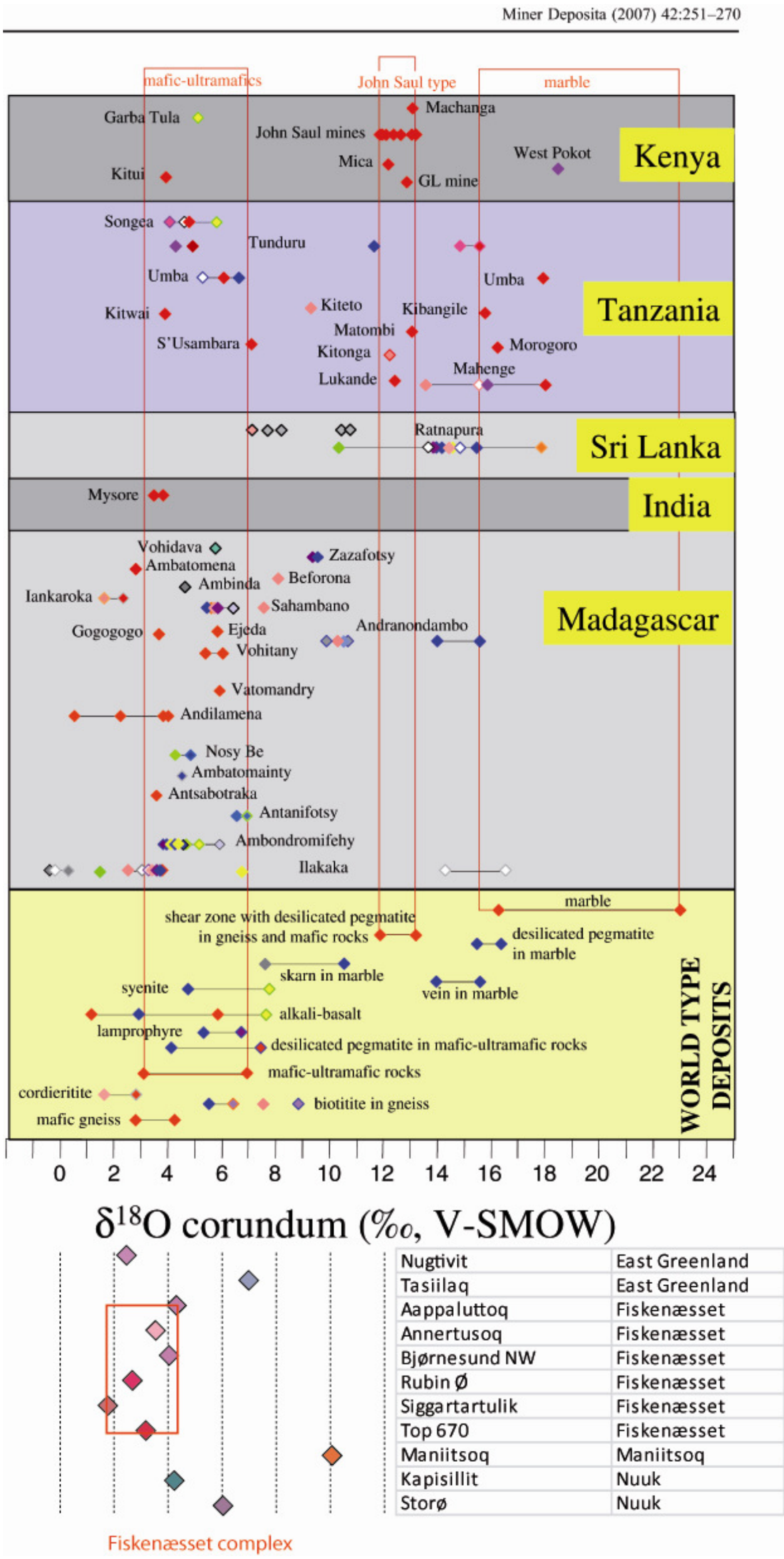


Figure 4: Oxygen isotope values of corundum from world-wide deposits after Giuliani et al. (2005, 2007); Figure modified from Giuliani et al. (2007).The new oxygen isotope data for the samples from Greenland is plotted beneath applying the same scale. A red box indicates the range of values for the Fiskenæsset complex. Colours in the diamonds represent the approximate colour of the corundum. Figure copied from Kalvig & Keulen, 2011.

However, the fact the these samples from Aappaluttoq overlap more strongly with samples from Longido (Tanzania), Winza (Tanzania), Chanthaburi (Thailand) and Ilalaka (Madagascar) than with other samples from some areas in the Fiskenæsset complex, and even with some of the samples from Aappaluttoq, indicates the need for further study of international samples from mafic-ultramafic occurrences. It is very well possible that other localities exist, with a fingerprinting signature that is very similar to Aappaluttoq.

The best possibility to separate out the results for samples from Aappaluttoq versus these overlapping and similar international occurrences is, apart from this principle component analysis, a ternary diagram of Cr/Fe vs Si vs Ti/V/Ga or of Fe vs Cr/Si vs Ti/V/Ga (see Fig. 5). These three groups define the axes of the principle component diagram (Fig. 3).

It needs to be emphasized that the analysis for many samples, especially from the international occurrences, often is based on one or two values only and that not much literature data with geochemical results exists. To obtain better and more certain results, the dataset needs to be extended with more analyses.

Ruby/sapphire samples from Storø show a strong overlap in their geochemical signature with samples from Jaipur-Mysore (India), John Saul mine (Kenya), Mong Hsu (Myanmar), Sahambano (Madagascar), and Soamiakatra (Madagascar). With a further investigation of the higher order components (PC3, PC4 etc.) these samples can possibly be separated out. Mong Hsu and John Saul mine have for example much higher $\delta^{18}O$ values than the other samples, Sambano has low Ti concentrations, while Soamiakatra is much richer in iron than the other samples.

The ruby/sapphire samples from Maniitsoq have a unique position in the principal component plot. Their most significant neighbours are the sample from Tsavo, and the sample from Sri Lanka that might originate from Pelmadulla.

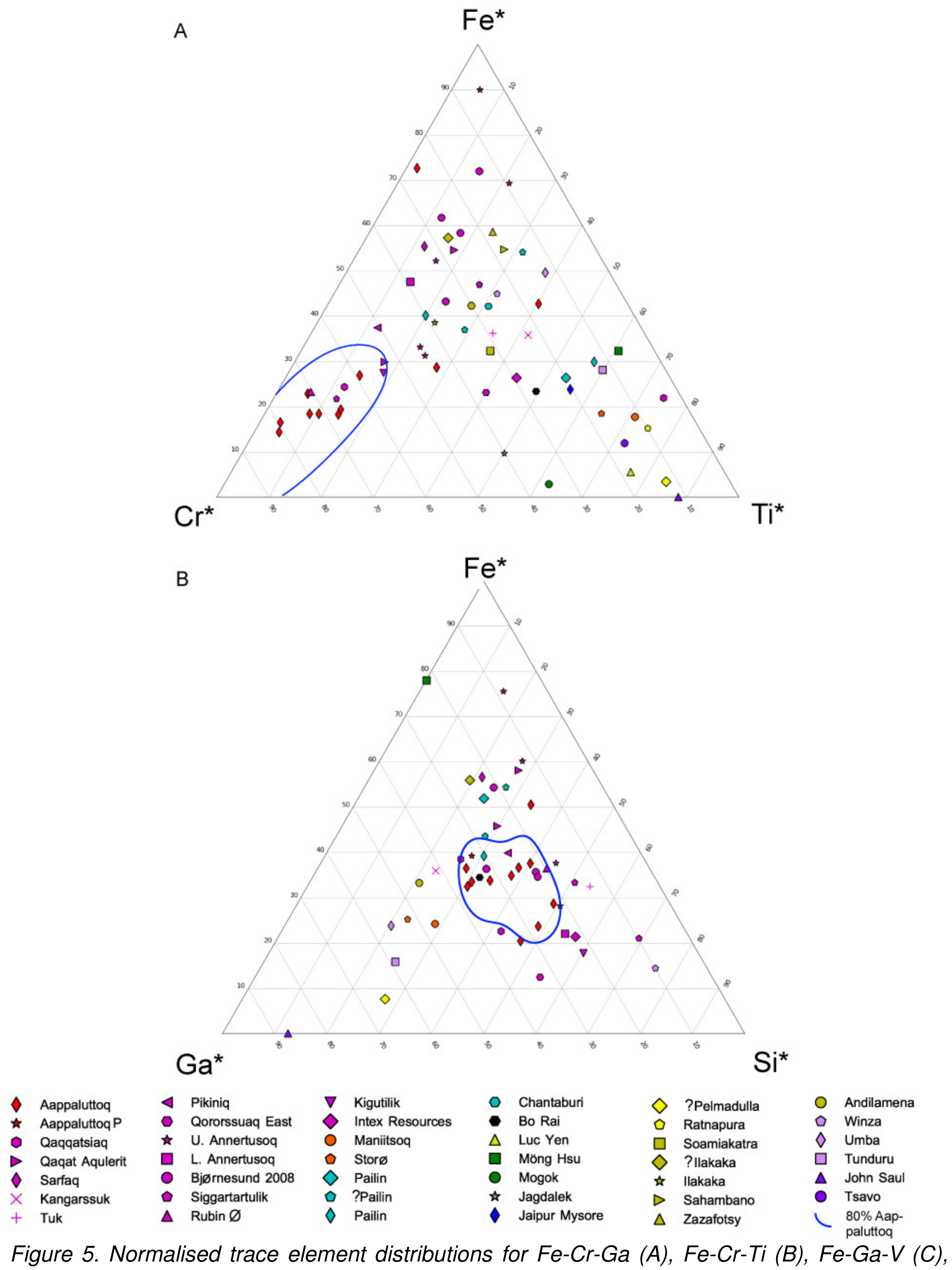


Figure 5. Normalised trace element distributions for Fe-Cr-Ga (A), Fe-Cr-Ti (B), Fe-Ga-V (C), Fe-Si-Ga (D), Ti-Cr-Ga (E), and Ti-Cr-V (F) in ruby from Aappaluttoq, the remaining Fiskenæsset complex, elsewhere in Greenland (in red and pink), and ruby from non-Greenlandic occurrences (Thailand-Cambodia in light blue, Western Thailand in black, Vietnam in light green, Myanmar in dark green, Afghanistan in olive green, India in dark blue, Sri Lanka in yellow, Madagascar in ocre, Tanzania in pale violet, Kenya in dark violet). The data is compared to literature data (Calligaro, 1999; Calvo del Castillo, 2009; Rakotondrazafy et al., 2008; Schwarz et al., 2008). Different colours indicate different countries. See text for further explanation of the blue lines. This Figure is a summary of Figure 3 in Keulen & Poulsen (2014).

3. Inclusions and internal features in Fiskenæsset corundum samples

3.1 Introduction

Inclusions and internal features are small entrapped crystals, impurities or fluid phases that were incorporated in gemstones and other minerals during their formation. The type of inclusions is closely associated with the geological history of the gemstones and their host rocks and therefore typical inclusion and internal features can be used as one of the methods to fingerprint the origin of a gemstone of unknown geographic setting. Inclusions and other internal features in corundum and other gem-stones are studied for two reasons. Firstly, they help to discriminate between natural stones, natural treated stones and synthetic ones, where all types have their own typical inclusions. Secondly, typical inclusions can help to identify the origin of a number of natural gemstones.

Here, we aim to show a series of characteristic inclusions and internal features for corundum samples collected in the Fiskenæsset complex. Most features have been observed in several samples from this area.

3.2 Photomicroscopy Methods

The investigations were performed on material collected in the Fiskenæsset complex during fieldwork in 2011 (Kalvig & Keulen, 2011). Single grains of raw corundum were picked after carefully crushing part of the hand specimen with a jaw crusher. Most of the investigated grains have a colour ranging from moderate- deep- to very deep- dark purplish red, and to greyish and dark purplish pink. The grains were examined using an optical Leica M8 stereoscopic microscope at GEUS and the Leica Application Suit version 3.7.0 software. The investigated samples were not polished, but small, naturally-formed 'windows' (flat crystal surfaces) in the grains have been used to study the inclusions and internal features of the Fiskenæsset corundum samples.

3.3 Results

A series of mineral inclusions and other internal features is very typical for the investigated samples from the Fiskenæsset complex. Figure 6 shows a series of common mineral inclusions like phlogopite (Fig. 6a), amphibole (anthophyllite; Fig. 6b), spinel (Fig. 6c), and rutile (Fig. 6d). Zircon and possible apatite (Fig. 6e-6f) occur less frequently, but still in several samples. Alternatively, the small minerals in Fig. 6e could be anorthite feldspar.

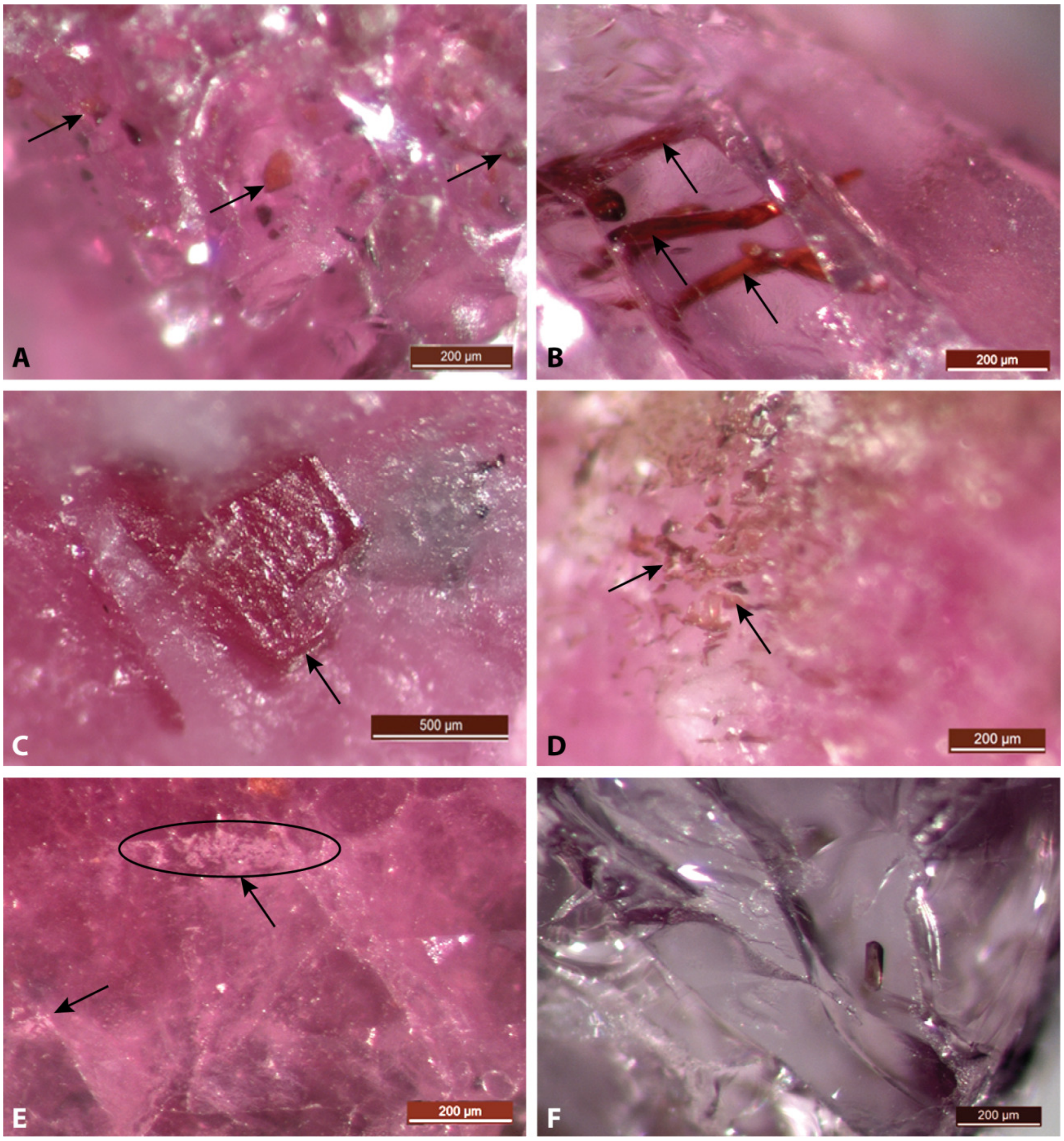
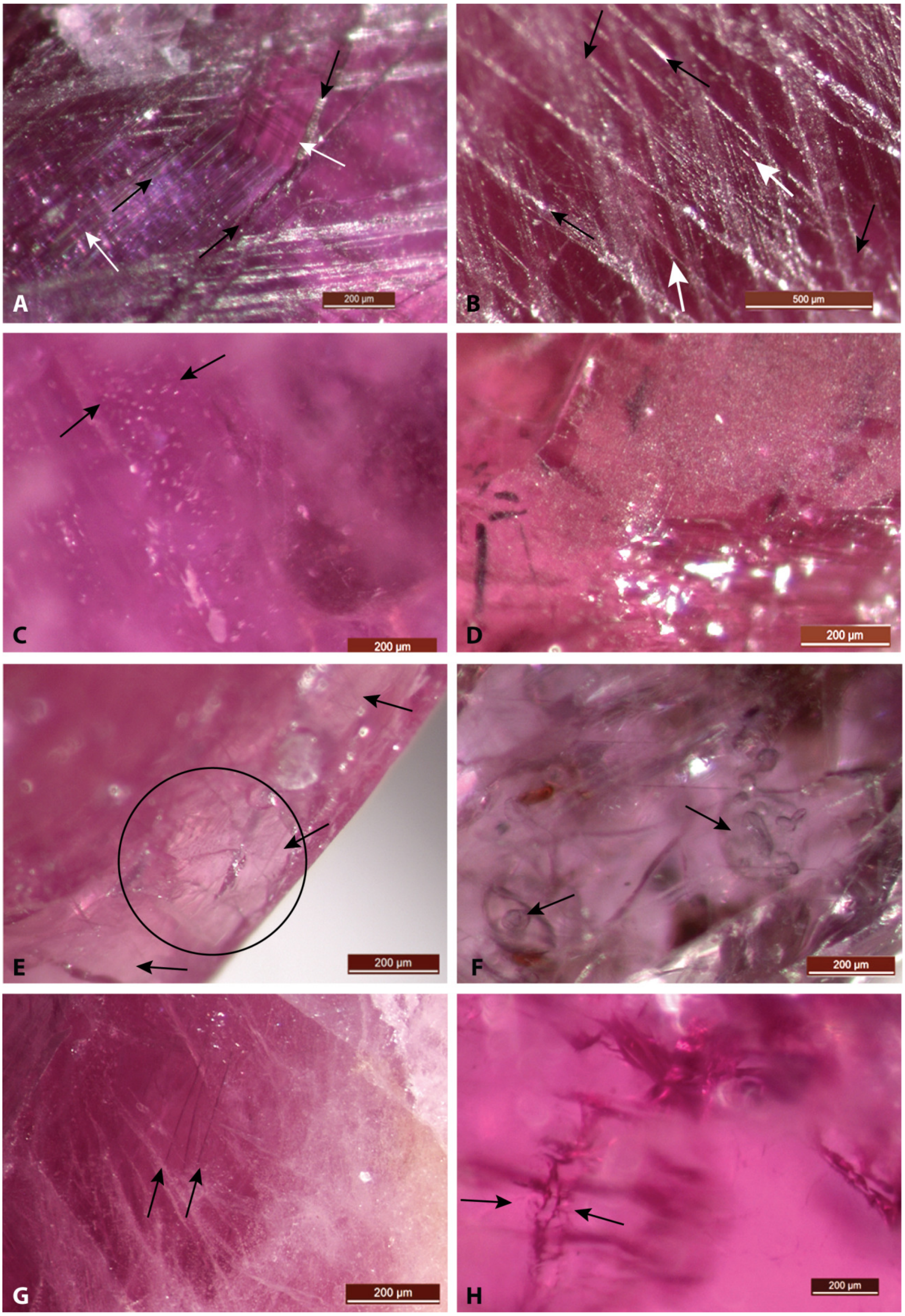


Figure 6. *Typical mineral inclusions in Fiskenæsset corundum stereomicroscope photographs. A: Reddish brown, tabular, hexagonal, partially translucent phlogopite minerals; sample 521152. B: Elongated brownish amphibole, most likely anthophyllite, sample 521131. C: Dark-red mineral, presumably spinel, sample: 521159. D: Stubby, dark orange to black rutile minerals, sample: 521160. E: Tight clusters of very small ?zircon crystals, sample 521123. F: Smokey transparent mineral, probably apatite or zircon, sample 521104.*

Other internal features than mineral inclusions occur in the Fiskenæsset corundum and can be seen in Figure 7. A special type of growth pattern,referred to as growth zoning, is a common feature in the Fiskenæsset corundum (Fig. 7a). The feature originates from small variations in concentrations of various building components during mineral growth and is often taken as an indication that the corundum is natural grown (GIA 2003). In the same figure fine dispersed rutile needles can be seen, another common feature in the Fiskenæsset corundum (e.g. Fig. 7a-7b).


A
200 µm
B
500 µm
C
200 µm
D
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E
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F
200 µm
G
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H
200 µm

Figure 7 (previous page). *Typical internal features in Fiskenæsset rubies; stereomicroscope photographs. A: Growth Patterns (parallel to black arrows) and cross-cutting rutile needles (white arrows), sample 521152. B: Rutile needles (white arrows) parallel to milky zones (downward pointing black arrows) and arrays (upward pointing black arrows), sample 521159. C: Negative crystals, sample 521104. D: Healed fracture, also called fingerprint inclusion consisting of tiny included crystals, negative crystals and milky zone, sample 521151. E: Zonal clouds with finely dispersed white material, sample 521160. F: Multiphase inclusions (fluid and solid inclusion in two or three phases), sample 521132. G: Irregularly oriented tubules filled with an unknown phase (?rutile or boehmite), sample 521108. H: Secondary feathers growing away from needles or former fractures, sample 521120.*

Parallel to these rutile needles arrays of small inclusion and milky zones consisting of finely dispersed fluid or solid material can be observed (Fig. 7b). Negative crystals (cavities in the crystal structure with the same shape and habit as the host crystal during its cooling), often with trapped fluids inside, commonly appear in the Fiskenæsset corundum (Fig. 7c). A combination of these features, included crystals, milky zones and negative crystals in a healed fracture can create a feature called fingerprint inclusion (Fig. 7d) (GIA 2003). Figure 7e shows a zonal cloud, which is a type of milky zone with finely dispersed material. Fluid inclusions and combined fluid-solid inclusions trapping two or three phases are rather common in Fiskenæsset samples (Fig. 7f). Two less common phenomena are shown in the last two photographs, the first being a series of irregularly oriented tubules that are filled with a solid material (Fig. 7g), the second being small secondary material that form feathers that grow away from needles or healed fractures in the crystal structure (Fig. 7h). In both cases the included material might be boehmite or rutile.

3.4 Discussion

One of the interesting observations on the mineral inclusions is the presence of brown amphibole inclusions in the samples. Even though no Raman investigations have been performed, it is most probably that this brown amphibole is anthophyllite. Anthophyllite has been observed as mineral inclusion in the Fiskenæsset complex corundum with the SEM (Keulen & Kalvig 2013) and in hand specimen collected in complex (e.g. Schumacher et al. 2011). Amphiboles, and especially the reddish brown anthophyllite in the Fiskenæsset samples, are relatively seldom occurring mineral inclusions in international ruby occurrences. Amphibole inclusions are known from mafic-ultramafic host-rock derived occurrences in, among others, Montepuez, Mozambique, Longido, Msinji & Winza, Tanzania and several places in Madagascar. Often these amphiboles are more green or black in colour. Green-black pargasite is noted occasionally as well in the marble-hosted rubies from Mogok, Myanmar and the Hunza Valley, Pakistan (Gübelin & Koivula 2008). Note however, that pargasite (a green amphibole) and gedrite (a black amphibole) are also observed as inclusions in Fiskenæsset rubies (Keulen & Kalvig 2013). Anthophyllite inclusions are not described in the very comprehensive atlas of Gübelin & Koivula (2008).

Similarly, phlogopite was observed as an inclusion in many samples from the Fiskenæsset complex (Fig. 6a) and this mica is often tabular shaped and reddish brown in colour, however near-black phlogopite has also been observed. Similar reddish brown phlogopite inclusions have for example been observed in samples collected in Luc Yen, Vietnam, Mogok, Myanmar, Tanzania, (Gübelin & Koivula 2008), Chimwadzulu, Malawi (Smith 2014) and the Hunza Valley, Pakistan (Gübelin 1982).

Rutile is the most common mineral inclusion in natural rubies and it is common in the Fiskenæsset samples as well, as individual grains, in needles and possibly in tubules. In some other areas it shows typical growth features like cross hatching or finely-spaced silk, however these features are not commonly observed in the Fiskenæsset samples. Secondary feathering from boehmite needles (Fig. 7h) was also observed in samples from Mogok, Myanmar (GRS 2015), but is only rarely seen in Fiskenæsset corundum.

Small aggregates of minerals, most likely zircon, but possibly anorthite, have been observed in several samples from the Fiskenæsset complex. Small zircon and anorthite inclusions have been described previously for the Fiskenæsset complex corundum samples (Keulen & Kalvig 2013). Similar clouds of fine-grained zircon have been described for rubies from Mangari, Kenya (Smith 2014), but anorthite has only been described as an inclusion mineral for rubies from Ruyil, Nepal (Gübelin & Koivula, 2008).

Straight growth zones with angular intersections, slight colour variations due to minor trace element ratio variations and cross-cutting net-shaped rutile needles are all features that are indicative of a naturally grown ruby. Other types of growth patterns however, can indicate synthetic crystals or assembled crystals. Growth patterns like those shown in Figure 7a are known from a small range of occurrences like Mong Hsu, Myanmar (Smith 2014), Umba Valley, Tanzania and Vatomandry, Madagascar (Gübelin & Koivula, 2008). Similarly negative crystals are rather commonly found in e.g., Mangari, Kenya (Smith 2014), in Mogok, in various magmatic rubies like Bo Rai and Chantaburi, Thailand, and in Sri Lankan rubies (Gübelin & Koivula, 2008).

Streams, flakes, milky zones and zonal clouds consist of finely dispersed material, which very often are dispersed rutile crystals. Zonal clouds are reported for rubies from Mangari, Kenya, while milky zones more often occur in, among others, Vietnamese ruby occurrences (Smith 2014).

Fluid inclusions and fluid-solid multi-phase inclusions are interesting features that allow to study the geological conditions during the entrapment of the fluids and/or solids.

3.5 Conclusions on the study of mineral inclusions and other internal features of corundum

Mineral inclusions and other internal features of corundum can be a helpful tool to characterise the origin of corundum. However, for a good geographic 'fingerprinting', a range of features need to be observed and registered, observations that however often are missing in the case of gem-quality samples. A combination of independent geographical 'fingerprinting' methods, such as LA-ICP-MS trace element analyses and the study of inclusions and internal features, will improve the chance of success.

Mineral inclusions of reddish-brown anthophyllite are rather uncommon in gem-quality ruby, as only a few amphibole-bearing localities globally are producing gem-quality stones, and the amphiboles from these locations more often are greenish or black. Similarly, phlogopite is not a very common mineral inclusion in rubies globally, although it is observed more often than anthophyllite. As both anthophyllite and phlogopite are rather common as inclusions in the Fiskenæsset rubies, they are important indicators for a Fiskenæsset origin.

Growth patterns, dispersed clouds of small zircon grains, zonal clouds and milky zones are distinguishing features for Fiskenæsset corundum, as are secondary feathering from ?boehmite needles.

The quality of the observations would improve from using cut and polished samples instead of raw stones.

4. Coloured stones gemmology course in Dubai

As part of the GEUS knowledge building into gemstones, Majken D. Poulsen attended the “Colored stones” gemmology course in Dubai 16-27th November 2014 at the International Gemological Institute. The course was a total of 10 days, and the following subjects were introduced:

- Introduction to basic terms in gemmology
- Use of various gemmological instruments to identify gemstones
- Origin determination by study of gemstones inclusions
- Ruby, sapphire, emerald, tanzanite, quartz, peridote, turquoise, tourmaline and more
- Ornamental gemstones and rare gemstones
- Treatments and synthetics

The course had both theoretical and intensive lab sessions with various gemmological instruments and more than 100 different coloured stones were presented.

5. The GIT 2014 conference

The Gemmological Institute of Thailand (GIT) 2014 conference was held 8th -9th of December 2014 and two fieldtrips were placed before and after the conference, respectively. The conference was in Chang Mai in Thailand, and the pre-conference excursion was a 5-days trip to Mogok in Myanmar (Figure 8). Majken Poulsen attended the pre-conference excursion and the conference together with the geologists Anette Juul-Nielsen and Helene Heide-Jørgensen from Ministry of Mineral Resources at the Government of Greenland. The Mogok field trip covered three days of excursions to different mines, temples and local gemstone markets. The mines visited were in West, East and North Mogok. Most of the mines visited were open pit mines, but a few had some underground mining too. The machinery was very primitive and no big bulldozers or other machines were observed in the mines. Most of the work was carried out by hand including digging and rinsing the carbonate-rich soils.

Several local gemstone markets were visited (Figure 8), where the people from Mogok sell their stones to each other, but the mines often have auctions and sell in bigger quantities to local people or to companies.

Figure 8. *Impression from Mogok. A)Open pit mine for ruby and red spinel in Bhone Myint Aung mine. B) The result of one week's work of rubies and other precious gemstones from the mine Yadana Shin Gems Co. Ltd. C) The workers are searching for gemstones in the crushed gravel in Yadana Shin Gems Co. Ltd. D) Sorting and preparing sapphires for sale or cutting and polishing in the Bawmar Sapphire Gem Processing.*

6. Overview of the appendices

- Extended peer-reviewed abstract of Poulsen & Keulen for the GIT 2014 conference in Thailand
- PDF of the poster presentation of Poulsen & Keulen at the GIT conference in Thailand.

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Comparison on the geochemical methods for fingerprinting of Greenlandic gem-corundum (rubies)

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Extended Abstract

Since the 1990's there has been considerable interest in investigating and exploiting the Greenlandic gemstone deposits with corundum (sapphire and ruby) at Fiskenæsset in southern West Greenland and the Greenlandic Ministry for Industry and Mineral Resources (MIM) have issued a number of exploration and small scale licenses for the occurrences. The corundum is sitting in an extensive area measuring 30 by 70 km in the Fiskenæsset anorthosite complex (Windley et al, 1973; Myers, 1985), which is part of the Archean basement in Greenland. The area contains more than 40 ruby localities and a few of those are well-developed and host gem-quality corundum.

Other Greenlandic ruby localities are found in West Greenland in the area around Maniitsoq and Nuuk. Rubies are also found in South-East Greenland in the Tasiilaq area. The ruby localities in Greenland known so far are concentrated in the North Atlantic Craton, mainly near anorthosites, amphibolites and ultramafic bodies and are often related to intruding felsic sheets.

The company True North Gems Greenland (TNGG) has sought an exploitation license in Fiskenæsset complex at one of the ruby localities called Aappaluttoq (Greenlandic for 'the red'). The research is collaboration between MIM and GEUS, and involves geochemical study of the Greenlandic corundum, with the purpose of finding good characteristics for recognizing the rubies from Aappaluttoq with a precise and non-destructive analytical method.

Here, we will describe results for LA-ICP-MS analyses and µ-XRF analyses. Major elements in rubies are Al and O, but 22 trace elements were investigated with LA-ICP-MS, where only Mg, Si, Ti, V, Cr, Fe, and Ga yielded significant results. These seven trace elements gave important characteristics for the Fiskenæsset rubies that can be differentiated from the other Greenlandic occurrences (Kalvig & Keulen, 2013).

The samples from Fiskenæsset are lower in Ti, Fe and V and higher in Cr compared to the other samples from Greenland. The Aappaluttoq samples have a very high Cr content (up to 16000 ppm) and are low in

Mg, Ti and Fe. The rubies from other Fiskenæsset localities show a strong resemblance to rubies from Aappaluttoq, when compared to other Greenlandic ruby occurrences

The Aappaluttoq rubies have been compared to international occurrences and are distinguishable from other ruby localities especially in ternary diagrams such as a Fe-Ti-Cr or Fe-Ga-Cr diagram (Figure 1). The samples from Aappaluttoq show only minor overlap with literature data on samples from other international localities, like Pailin, Bo Rai, Longido, Winza, and a number of occurrences in Madagascar. Rubies from these occurrences are all set in, or derived from, mafic or ultra-mafic rocks (Keulen & Poulsen, 2014).It is therefore important to analyze more samples from mafic-ultramafic ruby occurrences for comparison and thereby defining a good geochemical fingerprinting of the Aappaluttoq rubies.

In order to find a more non-destructive method for the analysis of rubies we compared micro-X-ray fluorescence (µ-XRF) to LA-ICP-MS analyses. µ-XRF is an elemental analysis method, which can examine very small sample areas. It uses direct X-ray excitation to induce characteristic X-ray fluorescence radiation from the sample for elemental analysis. Unlike conventional XRF, µ-XRF uses X-ray optics to restrict the excitation beam size or to focus the excitation beam to a small spot on the sample surface so that small features on the sample can be analyzed. A spatial resolution of down to about 10 micrometers can be reached. The µXRF instrument applied in this study is a Bruker M4 Tornado based at the Roskilde University.

The Greenlandic corundum samples from Aappaluttoq were analysed for the purpose of fingerprinting of the Aappaluttoq corundum and to compare the results to the analyses on corundum from other localities in the Fiskenæsset complex: Bjørnesund, Rubin Ø, Kigutilik, Upper Annertusoq and Lower Annertusoq. Investigations concentrated on the elements O, Mg, Al, Si, Ti, V, Cr, Fe. Results were compared to those obtained with LA-ICP-MS on the same grains in the same samples (Figure 2). µXRF analyses are standard-less analyses.

When comparing some of the analytical methods, it becomes evident that there are quite big differences in the accuracy of trace element content. As LA-ICP-MS analyses were performed with standards and tested on known unknowns, these results are considered more reliable. The difference in values obtained with LA-ICP-MS and µ-XRF is too large and the spreading in the µ-XRF measurements is too random to consider µ-XRF as a suitable tool for geochemical fingerprinting. The LA-ICP-MS is not entirely non-destructive, whereas the µ-XRF is non-destructive, but the obtained results for the two methods is makes the LA-ICP-MS the preferred analytical method (Keulen & Poulsen, 2014). Of all investigated analytical methods for characterizing the Aappaluttoq rubies so far, LA-ICP-MS has been the method, which gives the best possibilities for fingerprinting.

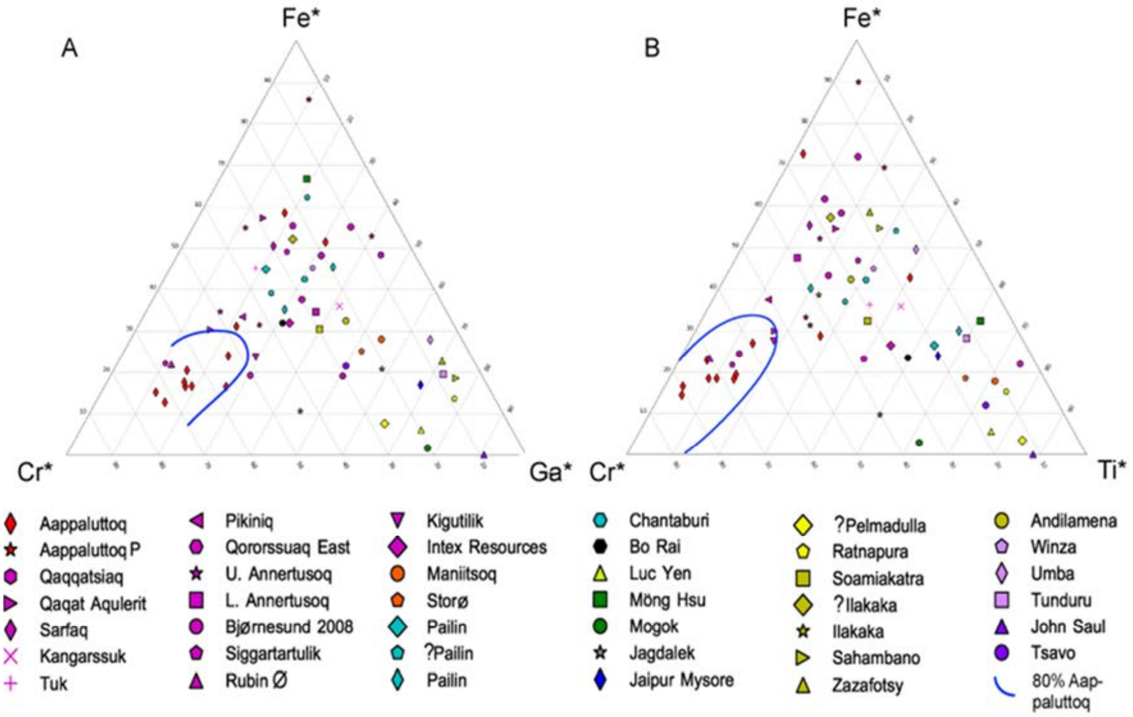

Figure 1: Normalized trace element distribution for Fe -Ga-Cr (A) and Fe-Ti-Cr (B). The Aappaluttoq samples are marked with a blue line. The Aappaluttoq samples are compared to international ruby localities (Calligaro, 1999; Calvo del Castillo, 2009; Rakotondrazafy et al., 2008; Schwarz et al., 2008).

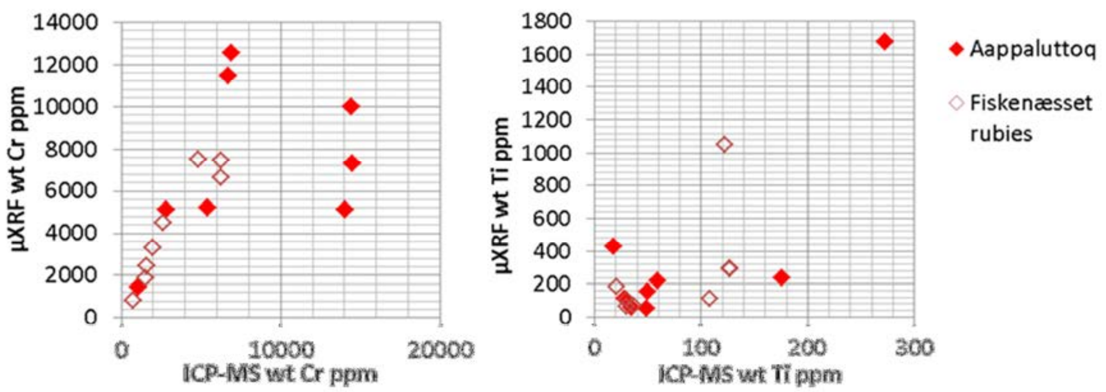

Figure 2: of the results from µXRF and LA-ICP-MS. Left: The average of Cr in ppm for the two different meth-ods. The differences between the measured element concentrations are not too divergent. Right: The average of Ti in ppm for the two different methods. The concentration of Ti measured with µXRF is about 4 times larger than with the LA-ICP-MS.

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Abstract
The geochemical fingerprinting of the rubies from Fiskenæsset reveal characteristic geochemical signatures with low Ti, moderate to low Fe content and high Cr content compared to the other samples from Greenland. Especially the The Aappaluttoq rubies have a very high Cr content and are low in Fe, Ti and V.

Introduction
Since the 1990's there has been considerable interest in investigating and exploiting the Greenlandic gemstone deposits with corundum (sapphire and ruby) at Fiskenæsset in southern West Greenland. The corundum is sitting in an extensive area measuring 30 by 70 km in the Fiskenæsset anorthosite complex (Windley et al. 1973; Myers, 1985), which is part of the Archean basement in Greenland. The area contains more than 40 ruby localities and a some host gem-quality corundum.
Other Greenlandic ruby localities are found in West Greenland in the area around Maniitsoq and Nuuk (figure 1). Rubies are also found in South-East Greenland in the Tasiilaq area. The ruby localities in Greenland known are concentrated in the North Atlantic Craton, mainly near anorthosites, amphibolites and ultramafic bodies and are often related to intruding felsic sheets.
In this study the Greenlandic corundum were analyzed for the purpose of fingerprinting of the Fiskenæsset corundum especially the rubies from the Aappaluttoq locality.

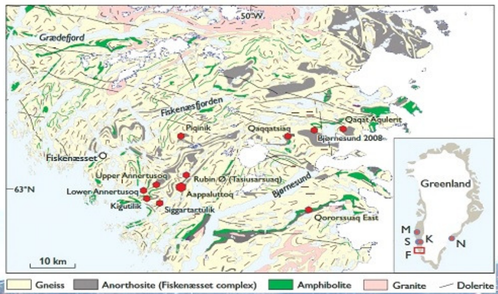

Figure 1: Simpified map of southern West Greenland showing the investigated area with pink and red corundum. The corundum localities marked on the map. Small map of Greenland high light The Fiskenæsset area with a red rectangle and other Greenlandic ruby occurrences; F: Fiskenæsset, M: Maniitsoq, S: Storø, K: Kapisillit, N: Nattivit. Map after Keulen & Kokfelt et al. (2011).

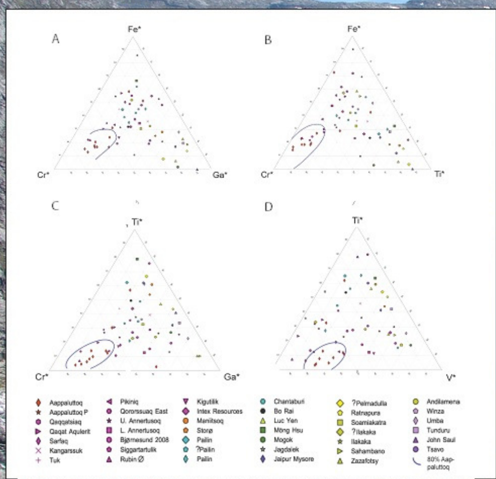

Figure 2: Normalized trace element distribution for Fe-Ga-Cr (A) and Fe-Ti-Cr (B), Cr-Ti-Ga (C), Cr-Ti-V (D). The Aappaluttoq samples are marked with a blue line. The Aappaluttoq samples are compared to international ruby localities (Calligaro, 1999; Calvo del Castillo, 2009; Rakotondrazafy et al. 2008; Schwarz et al. 2008).

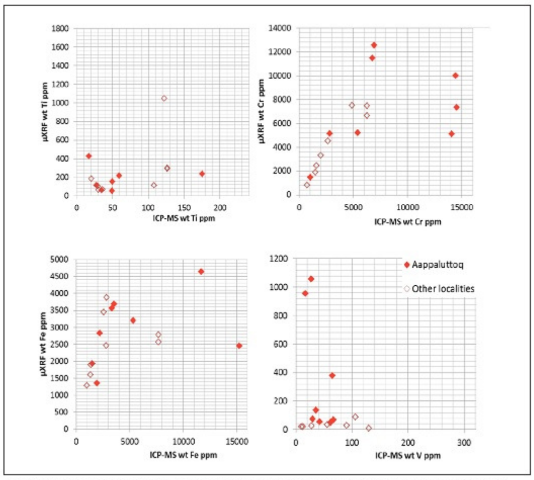

Figure 3: Comparison of the results from µXRF and LA-ICP-MS. The average of Ti, Cr, Fe and V in ppm for the two different analytical methods. The differences between the measured element concentrations are not too divergent. The concentration of Ti measured with µXRF is about 4 times larger than with the LA-ICP-MS. The LA-ICPMS gives results that are more reliable then the µXRF method. The Aappaluttoq samples are marked a red square and the empty squares are from corundum from other localities in Fiskenaesset area.

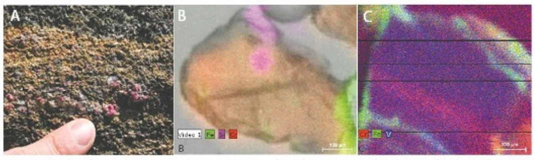

Figure 4: A) rubies from Tasiusarsuaq, Fiskenæsset. B) Image from the µXRF scan of a ruby grain from Aappaluttoq. An inclusion is visible with high Si, possible Anorthite. C) An scan from µXRF on a corundum from Maniitsoq showing chemical zonation in the grain. The Aappaluttoq rubies shows no chemical zoning in the grains. The µXRF is a good tool for providing a 2d image of geochemical element distributions.

Results and discussion
Major elements in corundum are Al and O, and Cr in corundum gives red color (ruby), all other colors are called different variations of sapphire (pink sapphire ect.). For the initial analysis 22 trace elements were investigated with LA-ICP-MS, where only Mg, Si, Ti, V, Cr, Fe, and Ga yielded significant results. These seven trace elements gave important characteristics for the Fiskenæsset rubies that can be differentiated from the other Greenlandic occurrences (Kalvig & Keulen, 2013).

The samples from Fiskenæsset are lower in Ti, Fe and V and higher in Cr compared to the other samples from Greenland. The rubies from Fiskenæsset localities show resemblance to rubies from Aappaluttoq, but Aappaluttoq rubies have very high Cr content (up to 16000 ppm) and low Mg, Ti and Fe. The Aappaluttoq rubies have been compared to international occurrences and are distinguishable especially in ternary diagrams such as a Fe-Ti-Cr or Fe-Ga-V diagram (Figure 2).

The samples from Aappaluttoq show only minor overlap with literature data on samples from other international localities, like Pailin, Bo Rai, Longido, Winza, and a number of occurrences in Madagascar. Rubies from these occurrences are all set in, or derived from, mafic or ultra-mafic rocks (Keulen & Poulsen, 2014).

When comparing LA-ICP-MS analyses and µ-XRF the differences are too large and spreading in the µ-XRF measurements too random to consider as a suitable tool for geochemical fingerprinting. The LA-ICP-MS so far gives the best results for geochemical fingerprinting of the Greenlandic corundum.

Further work will include analysis of high quality rubies, description of mineral characteristics and inclusions and analyzing samples from international mafic-ultramafic ruby occurrences for comparison and thereby defining a good geochemical fingerprinting of the Aappaluttoq rubies.