

# Report on the activities in the ruby project 2011-2013

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



**GEUS**

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# 1. Executive summary

This project on the evaluation of Greenlandic rubies is part of a collaboration project between the Ministry of Industry and Mineral Resources (MIM), Greenland, and the Geological Survey of Denmark and Greenland (GEUS), Denmark. The investigations are mainly aimed at the characterisation of the Fiskensæst complex rubies, because the most promising ruby outcrop in that area, Aappaluttoq, is likely to be mined in the nearest future by the company True North Gems Greenland (TNGG). In the third year of the three-year long project on Greenlandic rubies the activities concentrated on the analytical investigation of the rubies collected in the Fiskensæst complex in the summer of 2011 and on sapphire grains from other corundum outcrops in Greenland. Furthermore, it has been tried to apply other fingerprinting methods to the samples from the Aappaluttoq. This study focusses on ruby (red corundum), but also includes some data on sapphire (mainly bluish corundum).

In the summer of 2011 circa 50 rock samples from 8 localities in the Fiskensæst complex were collected with the aim to characterise the Fiskensæst complex ruby occurrences using gemmological, geochemical and optical investigations (see Kalvig & Keulen, 2011).

From the collected material 32 rock samples were selected. These samples were crushed and the rubies larger than 2 mm were collected and described for their colour, transparency, size and other characteristics (see Kalvig & Keulen, 2011; Keulen & Kalvig 2013). Five of these samples and twelve samples from the GEUS archives have been investigated with laser ablation sector-field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) at GEUS in order to investigate the trace element distribution. Furthermore, four Greenlandic sapphire localities have been reinvestigated after preliminary investigations by Kalvig and Frei (2010) in order to have the same analytical quality on all Greenlandic samples. Both sets, rubies and sapphires, were compared to samples from international occurrences. These investigations have been reported in Chapter 2.

Trace element investigations with a LA-SF-ICP-MS instrument appear to be a promising tool in the fingerprinting of the Greenlandic ruby. Based on the trace elements Si, Ti, Cr, Fe, and Ga for the highest quality samples from Aappaluttoq, it seems possible to distinguish these from 25 internationally known ruby occurrences. For a most effective fingerprinting a combination of trace element analyses, oxygen isotope analyses (see Kalvig & Keulen, 2011) and other studies need to be performed with for example multivariate statistics. It should be stressed that the ICP-MS study ought to be confirmed on gemstone quality rocks in the future, as trace element patterns are not exactly identical for low and high quality stones.

A blind test has been performed in order to investigate the limitations of fingerprinting the Aappaluttoq occurrence. The sample from the Aappaluttoq occurrence was recognised correctly in this test, as was another sample from the Fiskensæst complex.

The samples from Aappaluttoq, in contrast to most other localities in the Fiskensæst complex, are not very rich in mineral inclusions. Anorthite inclusions, when they are observed,

probably are a good characteristic of the Fiskenæsset rubies, as this type of inclusions does not occur often in rubies from other localities (Keulen & Kalvig 2013).

We performed Raman Spectroscopy analyses and fluorescence spectroscopy analyses at the Technical University of Denmark (DTU), which are reported in Chapter 3. Analyses were performed to characterise the Greenlandic rubies with a non-destructive method. Unfortunately, both spectrometry methods do not work very well on ruby samples that are relatively rich in the trace element chromium, as is the case for the Fiskenæsset complex samples and especially the Aappaluttoq sample.

The possibilities that the micro-X-ray fluorescence method provides to investigate corundum samples – element spot analyses and element mapping - have been tested on an instrument at the Roskilde University Center (RUC). The large advantage of the method is that it is non-destructive and works well on polished surfaces. Unfortunately, both techniques cannot be applied to the rubies from the Fiskenæsset complex. The data obtained in the spot analysis has a too low accuracy to be able to use as a fingerprinting tool. The samples from Aappaluttoq are not zoned and therefore did not yield a characteristic element map pattern that could be used to typify individual corundum crystals or the Aappaluttoq occurrence. A description of the micro-X-ray fluorescence method and the obtained results are given in Chapter 4.

A short summary of the earlier results for oxygen isotope analyses on rubies is given in Chapter 5. This is a useful method on raw corundum, but too destructive to be used extensively on polished stones.

Geochemical fingerprinting applying LA-SF-ICP-MS is so far the most promising method for fingerprinting samples. The method needs verification against true gemstone quality stones and a better comparison with samples from other, international occurrences. As geochemical fingerprinting applying LA-SF-ICP-MS is not entirely non-destructive, other possible methods need further investigation as well to establish the best, cheapest and least destructive method for determining the origin of polished stones.

## 2. Trace element geochemistry as a tool for fingerprinting rubies

### 2.1 Introduction

Ruby and corundum have the chemical formula  $\text{Al}_2\text{O}_3$  and usually includes very small quantities of other elements in its crystal structure, like most other minerals. The amount of these trace elements and their ratios depend on the geological conditions during the formation of the ruby and therefore vary between individual ruby deposits. Therefore, corundum trace elements can be used as a fingerprinting tool. The concentrations of 22 different elements in corundum were measured with laser ablation sector-field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS), however most investigated elements were not detected in the corundum samples. Trace element geochemistry investigations on the Greenlandic ruby and sapphires were concentrated on the elements Mg, Si, Ti, V, Cr, Fe, and Ga, as these elements were present in significant amounts and are the most widely reported ones in international literature as well.

### 2.2 Methods

Trace element concentrations of 22 elements in ruby and sapphire from Fiskenæsset, from other localities in Greenland, and from a few international occurrences, were determined on mineral separates by isotopic analyses using LA-SF-ICP-MS at GEUS. A UP213 frequency-quintupled Nd:YAG solid state laser system from New Wave Research (Fremont, CA), employing two-volume cell technology, was coupled to an ELEMENT 2 double-focusing single-collector magnetic SF-ICP-MS from Thermo-Fisher Scientific. The mass spectrometer was equipped with a Fassel-type quartz torch shielded with a grounded Pt electrode and a quartz bonnet. Operating conditions and data acquisition parameters are comparable to the settings used in 2012 (Keulen & Kalvig 2013).

The ICP-MS was optimised for dry plasma conditions through continuous linear ablation of the NIST 612 glass standard. The signal-to-noise ratios were maximized for isotopes in the isotopic middle and heavy mass range (i.e.  $^{49}\text{Ti}$  to  $^{208}\text{Pb}$ ) with simultaneous opting for low element-oxide production levels by minimising the  $^{254}\text{UO}_2/^{238}\text{U}$  ratios. Instrumental drift was minimised by following a double standard-sample-standard analysis protocol, bracketing 10 sample analyses by measurements of the BCR-2 basalt and the NIST-612 glass standards. The BCR-2 standard was used for Fe determination, and the NIST-612 glass standard for all other elements. The quality of the measurements was controlled by known-unknown analyses of the NIST-614 and NIST-612 glasses measured during the analytical sequence, yielding typical  $2\sigma$  accuracies of <18%, except for Mg (10-30%, depending on the concentration).

Data were acquired from single spot analysis of 25  $\mu\text{m}$ , using a pulse rate of 10 Hz and a nominal laser fluence of  $\sim 10 \text{ J/cm}^2$ . Total acquisition time for single analyses were  $\sim 80$  sec., including 30 sec. gas blank measurement followed by laser ablation for 30 sec. and

washout for 20 sec. Factory-supplied software from Thermo-Fisher Scientific was used for the acquisition of the time-resolved data, obtained through pre-set spot locations. Data reduction and determination of concentrations was calculated off-line through the software Iolite using the Trace\_Elements\_IS routine (Hellstrom et al. 2008, Paton et al. 2011).

23 ruby and pink sapphire samples and 8 sapphire samples were analysed (Table 1). Focus of the analyses was set to the following points: 1) strengthening of the signal from Aappaluttoq rubies and pink sapphires, 2) an investigation of samples from other outcrops in the Fiskenæsset complex, 3) a reinvestigation of the samples studied by Kalvig & Frei (2010), with the aim to analyse these Greenlandic samples at the same standard as the samples analysed in 2012 and 2013, and 4) a comparison to international occurrences. Each sample exists of 2-5 stones from the same outcrop and on these 25-30 spot analyses were made with the ICP-MS. The international samples were collected personally at the mining sites or were donated by a reliable source.

## **2.3 Results and discussion**

Analyses were performed on 22 different elements, however in most samples only 7 elements, apart from aluminium, were detected in significant amounts: Mg, Si, Ti, V, Fe, Cr, and Ga (see Figure 1). The elements Mn, Zn, Cu, Ge, Sr, Zr, Nb, Sn, Cs, Ba, La, Ce, Hf, Ta, and Pb are neither present in significant amounts in the Fiskenæsset rubies nor in the sapphires from Greenland. The Mg-concentration lies close to the detection limit of the ICP-MS system and these data therefore have a lower accuracy.

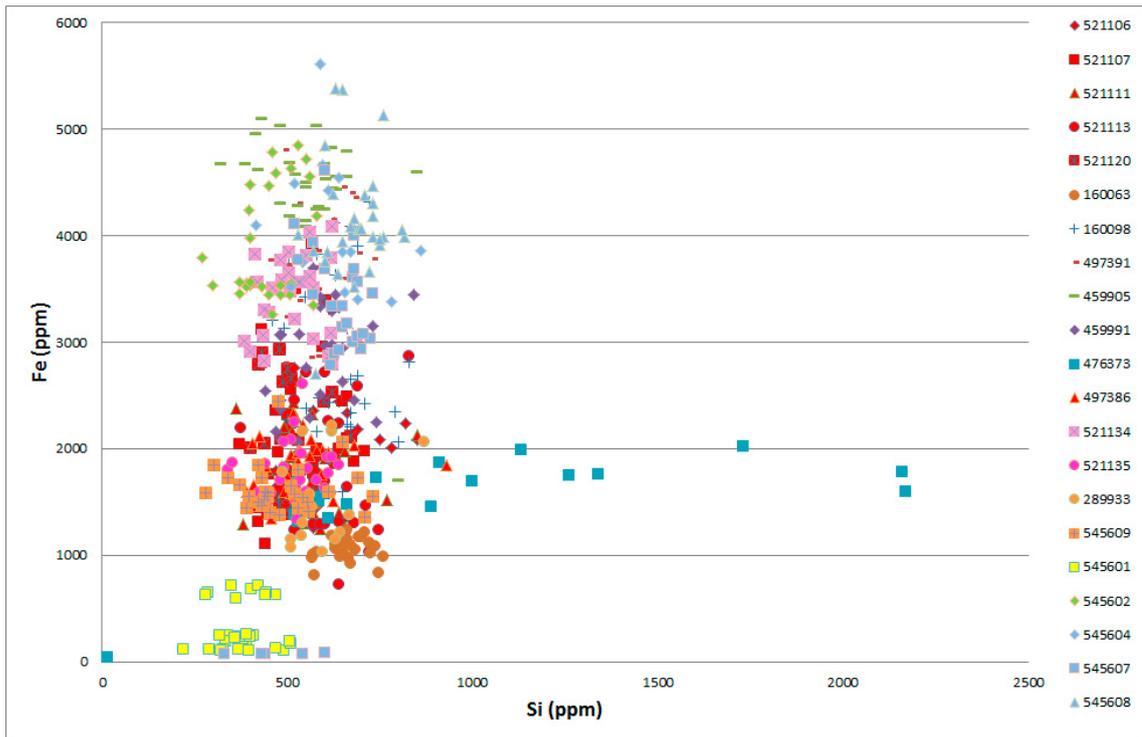
### **2.3.1 Rubies and pink sapphires**

The results for all ruby and pink sapphire samples investigated in 2013 are plotted in Figure 1. The Figure shows all analyses to give an indication of the spreading in the data, which is moderate to small for most elements in most samples. The samples from the Fiskenæsset complex in general, and from Aappaluttoq in particular, show high values for chromium, up to 16 000 ppm (sample 521106), and low values for Mg, Ti and Fe. Only the analysed sample from Sri Lanka (probably from Pelmadulla) is clearly lower in Fe, but has a higher Ti concentration. The investigated samples from Pailin are richer in Mg.

The normalised results for the investigations in 2013 on ruby and pink sapphire are plotted in Figure 2, showing all individual analyses on the stones. The data show that for the four different combinations of three trace elements, nearly no overlap occurs between rubies from Aappaluttoq and the investigated samples from elsewhere in Greenland, and from international occurrences. Some overlap of the Aappaluttoq samples occurs with the other areas within the Fiskenæsset complex, which is to be expected as the Aappaluttoq samples originate from the same area and were derived from the same kind of rocks.

Table 1: Samples analysed with ICP-MS in 2013. Colours are indicated after the GIA schedule ([http://www.gemval.com/color\\_grade.html](http://www.gemval.com/color_grade.html)).

| <b>GGU #</b> | <b>Country</b> | <b>Region</b>   | <b>Colour</b>           |
|--------------|----------------|-----------------|-------------------------|
| 521106       | Greenland      | Aappalutoq      | purplish red            |
| 521107       | Greenland      | Aappalutoq      | purplish red            |
| 521111       | Greenland      | Aappalutoq      | purplish red            |
| 521113       | Greenland      | Aappalutoq      | purplish pink           |
| 521120       | Greenland      | Aappalutoq      | purplish pink           |
| 160063       | Greenland      | Qaqqatsiaq      |                         |
| 160098       | Greenland      | Beer Mountain   |                         |
| 497391       | Greenland      | Beer Mountain   | greyish red             |
| 459905       | Greenland      | Sarfaq          |                         |
| 459991       | Greenland      | Kangarssuk      |                         |
| 476373       | Greenland      | Tuk             |                         |
| 497383       | Greenland      | Top 670         | reddish lilac           |
| 497386       | Greenland      | Top 670         | greyish red             |
| 521134       | Greenland      | Bjørnesund 2008 | Pink                    |
| 521135       | Greenland      | Bjørnesund 2008 | purplish red            |
| 289933       | Greenland      | Maniitsoq       | greyish magenta         |
| 545609       | Greenland      | Storø           | purplish pink           |
| 545601       | Sri Lanka      | ?Pelmadulla     | Purple                  |
| 545602       | Madagaskar     | ?Ilakaka        | Purplish red            |
| 545604       | Cambodia       | Pailin          | reddish orange          |
| 545606       | Cambodia       | Pailin          | reddish brown           |
| 545607       | Cambodia       | ?Pailin         | purplish red            |
| 545608       | Cambodia       | ?Pailin         | purplish red            |
| 224779       | Greenland      | Kapisillit      | turquoise grey          |
| 319411       | Greenland      | Ammassalik      | greyish magenta         |
| 497396       | Greenland      | Storø           | greyish magenta         |
| 497397       | Greenland      | Nattivit        | pale violet             |
| 497399       | Macedonia      |                 | greyish magenta         |
| 545603       | Thailand       | Chanthaburi     | bluish-white            |
| 545605       | Cambodia       | Pailin          | bluish-white            |
| 545612       | Cambodia       | ?Pailin         | blue, 3 polished stones |



A

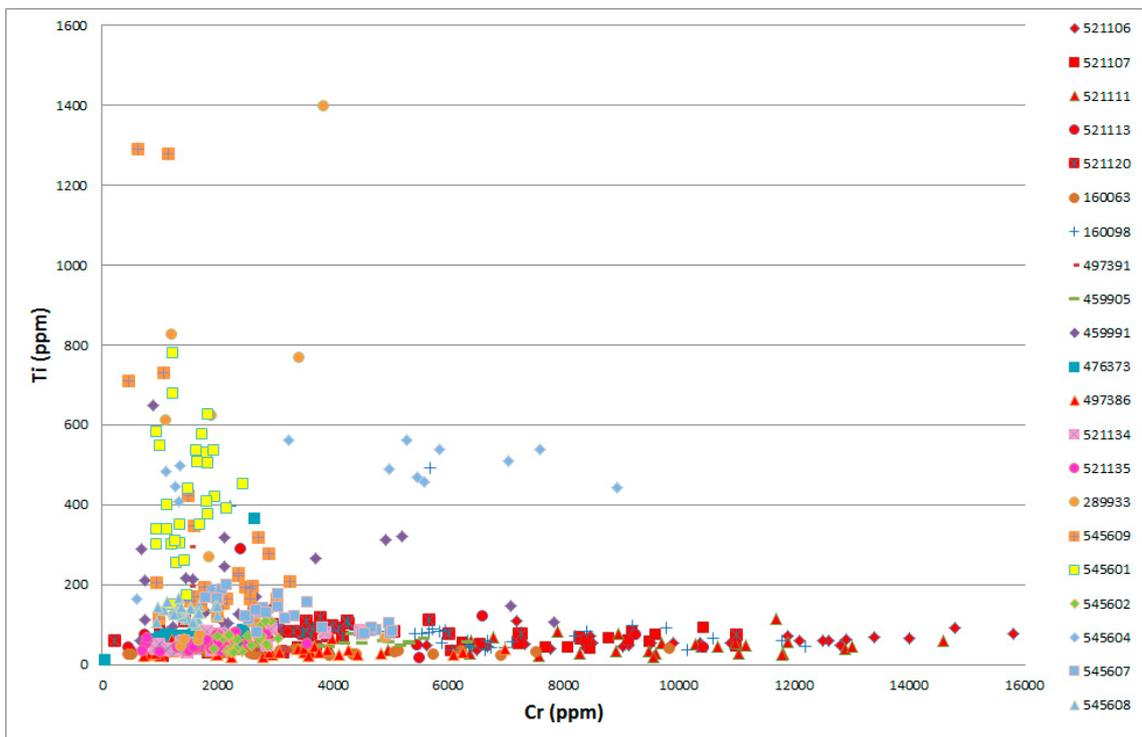
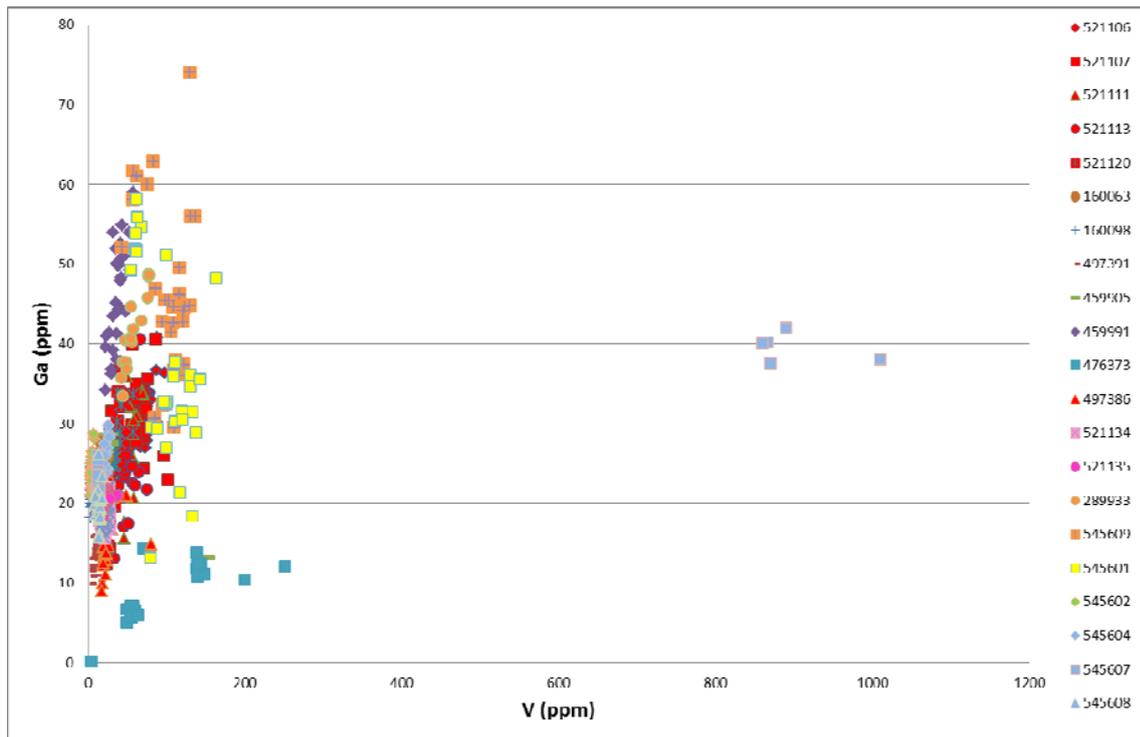
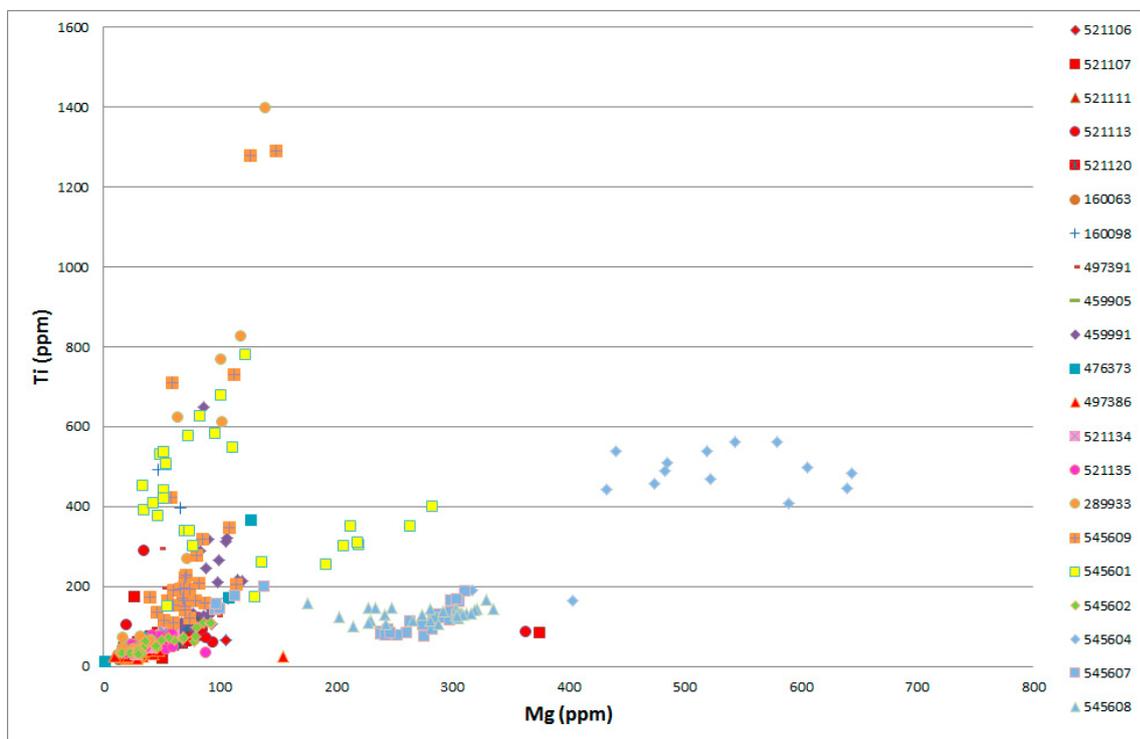


Figure 1 (this page and next). LA-ICP-MS data for individual analyses on the selected ruby samples. **A:** Fe vs Si, **B:** Cr vs Ti, **C:** Ga vs V, **D:** Ti vs Mg.

Figure 1  
continued:



C



D

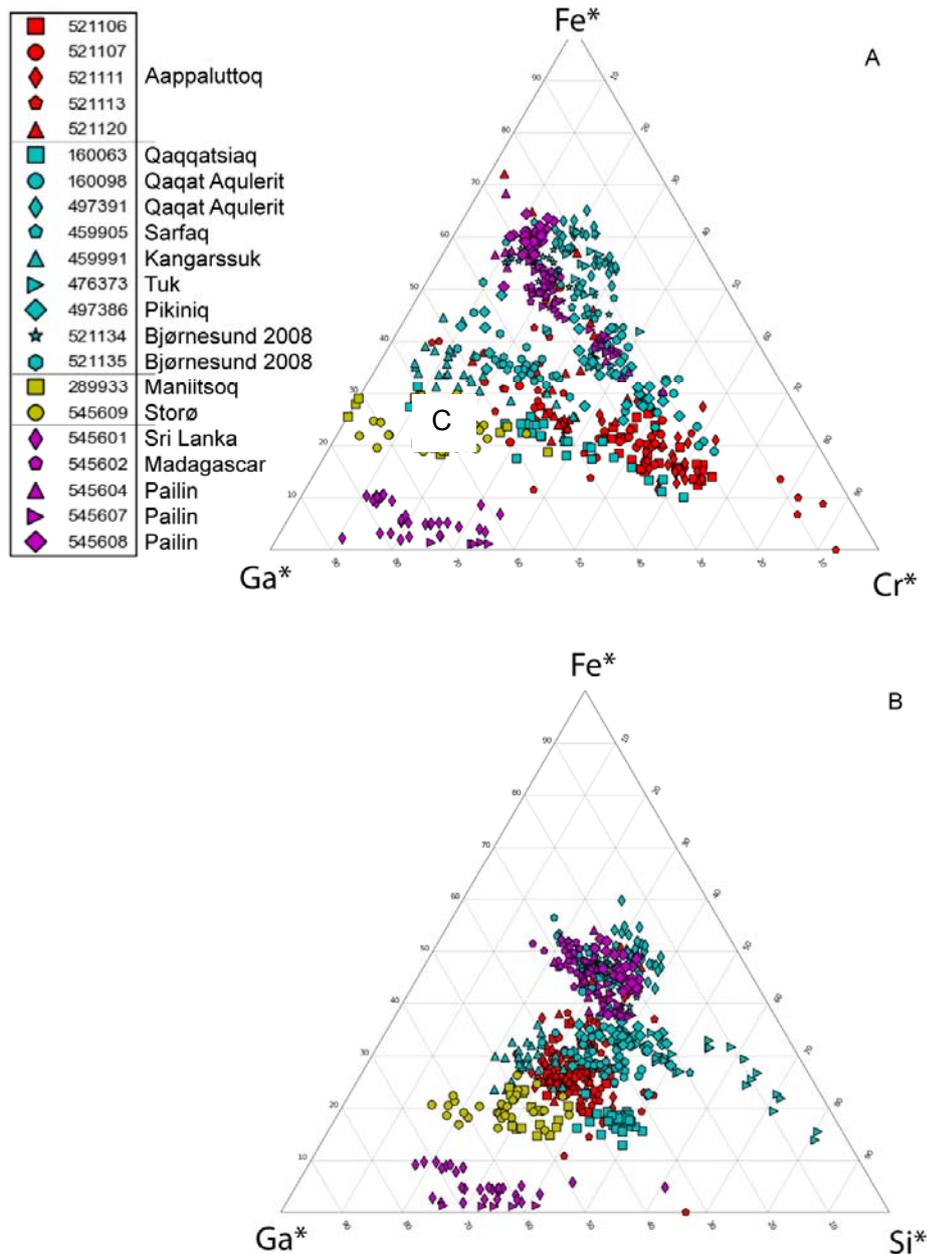
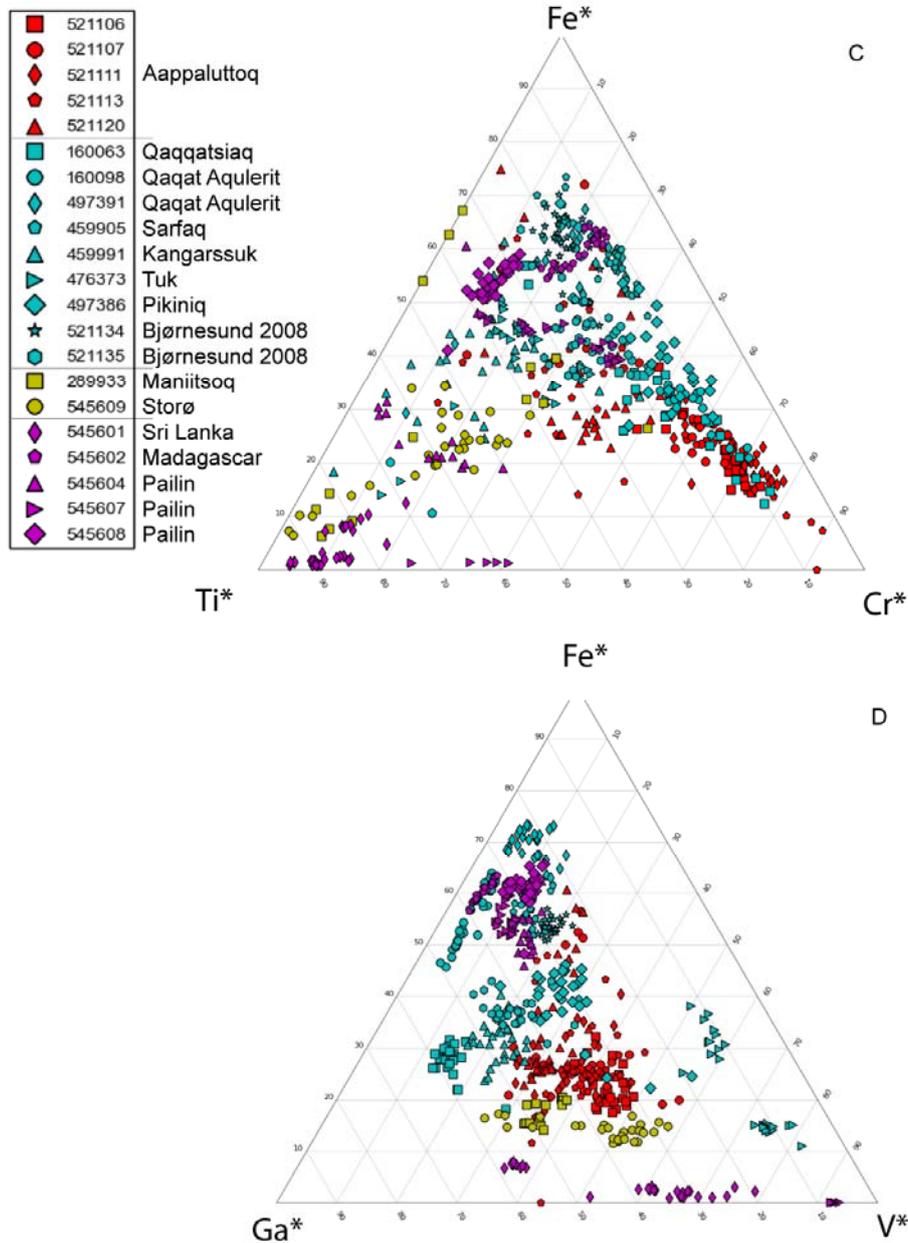


Figure 2 (this page and next). Normalised trace element distributions for Fe-Ga-Cr (A), Fe-Ga-Si (B), Fe-Ti-Cr (C), and Fe-Ga-V (D) in ruby and pink sapphire from Aappaluttoq, Fiskenæsset, elsewhere in Greenland, and from international occurrences. Different colours indicate these four different areas of origin. All ternary diagrams in this report were created with WxTernary (Keulen & Heijboer, 2011).

Figure 2 continued.



The average of the 25-30 spot analyses per sample is given in Figure 3. Here the analyses from 2013 are plotted together with those from 2012, and with data from literature on international occurrences. A blue line indicates the boundary of 80% of the ruby samples from Aappaluttoq (11 out of 14 samples). The figure shows only a minor overlap between samples from Aappaluttoq and other samples. Overlap occurs with several samples from the Fiskebøl complex – but not always with the same areas in all six ternary diagrams - with one sample from Pailin in two of the ternary diagrams, and with one sample from Bo Rai in one diagram. Thus these 80% of Aappaluttoq samples can effectively be sorted out

in these ternary diagrams, with respect to the other Fiskenæsset complex samples, and all studied international occurrences.

The Aappaluttoq samples that fall outside the blue line are in most cases samples 521109, 521110, and 521121. These samples are higher in Mg, Fe, and Ti than the other samples. They are also characterised by a high amount of inclusions and a milky (521109) to intermediate transparency (see Keulen & Kalvig, 2013). It is likely that these samples, apart from many SEM- and optically-detectable inclusions, have nanometre-sized inclusions that have put their mark on the ICP-MS analyses.

However, it needs to be stressed again (see Kalvig & Keulen 2011) that these ternary diagrams show normalised (relative) values only, and should be seen as a preliminary step towards a multivariate analysis. Furthermore, it is important to realise that many of the international samples were derived from a different geological setting (mainly marbles and xenoliths in basalts) and are therefore expected to have a different trace element signature. An investigation of additional ruby and pink sapphire samples from mafic and ultramafic rocks is therefore necessary to obtain a better certainty on the fingerprinting of Aappaluttoq rubies.

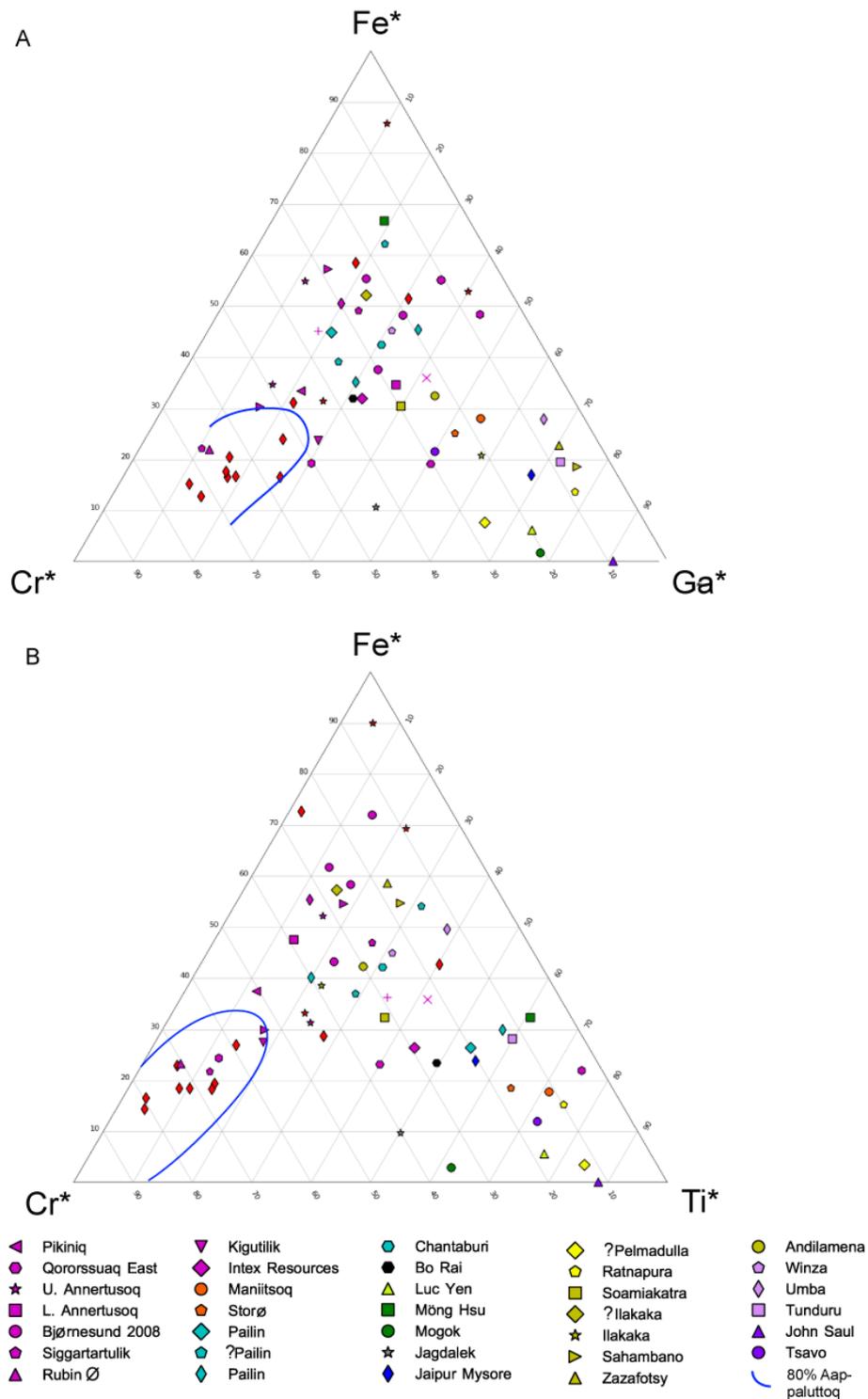


Figure 3 (this page and next two pages). Normalised trace element distributions for Fe-Cr-Ga (A), Fe-Cr-Ti (B), Fe-Ga-V (C), Fe-Si-Ga (D), Ti-Cr-Ga (E), and Ti-Cr-V (F) in ruby from Aappaluttoq, the remaining Fiskebøl complex, elsewhere in Greenland (in red and pink), and ruby from non-Greenlandic occurrences (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.

Figure 3 continued:

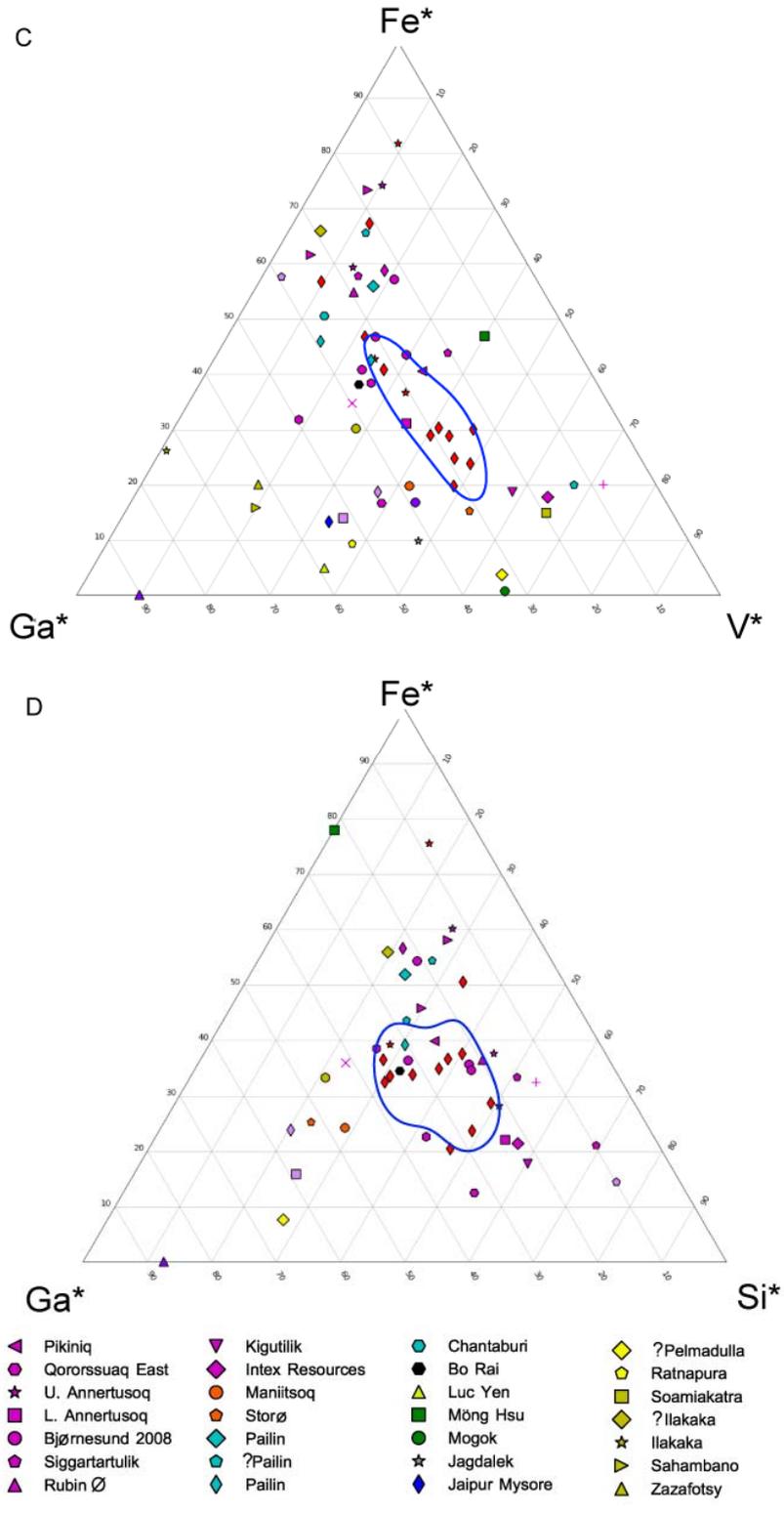
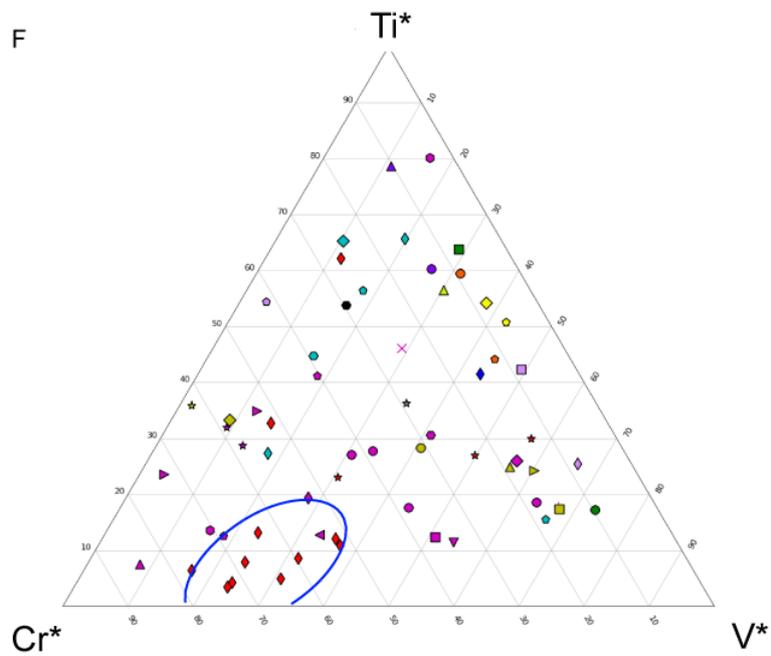
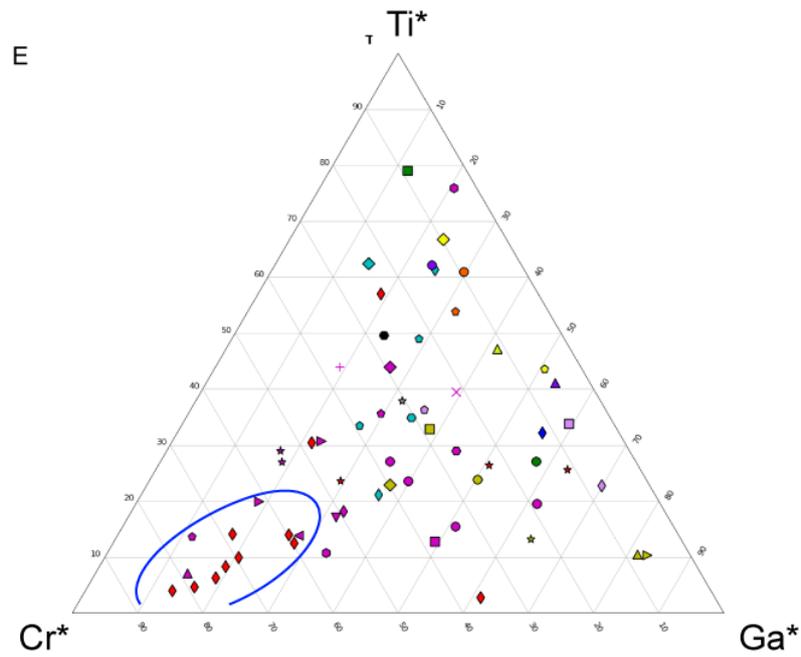


Figure 3 continued:



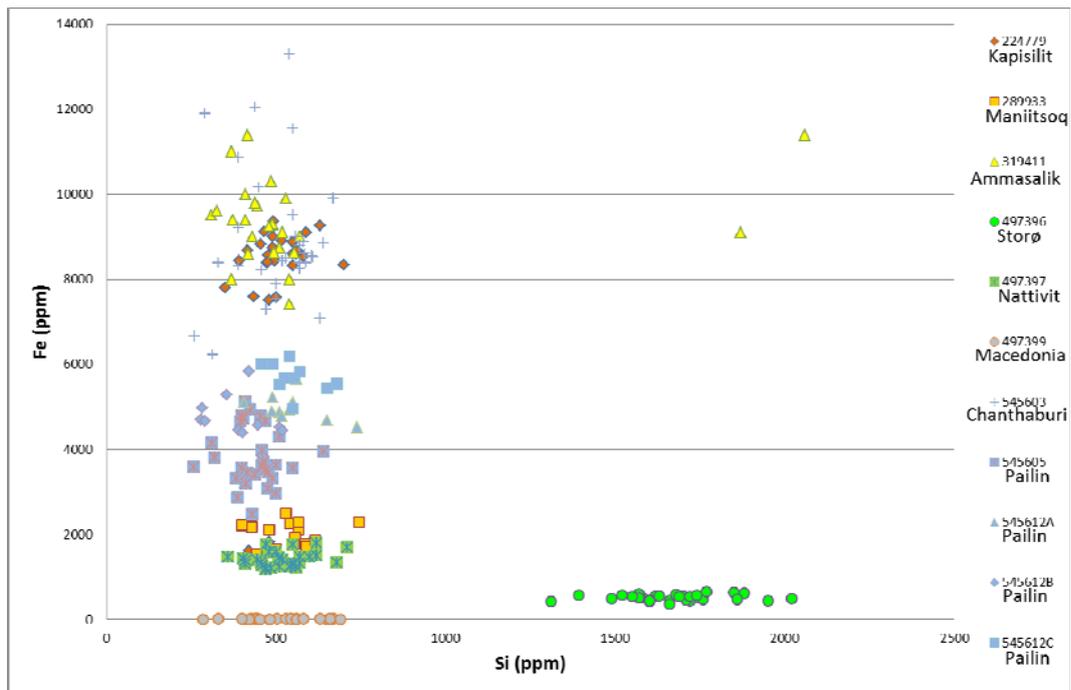
- |                  |                   |                   |                 |               |                   |
|------------------|-------------------|-------------------|-----------------|---------------|-------------------|
| ◆ Aappaluttoq    | ◀ Pikiniq         | ▼ Kigutilik       | ● Chantaburi    | ◆ ?Pelmadulla | ● Andilamena      |
| ★ Aappaluttoq P  | ● Qororssuaq East | ◆ Intex Resources | ● Bo Rai        | ● Ratnapura   | ● Winza           |
| ● Qaqqatsiaq     | ★ U. Annertusoq   | ● Maniitsoq       | ▲ Luc Yen       | ■ Soamiakatra | ● Uмба            |
| ▶ Qaqaq Aqulerit | ■ L. Annertusoq   | ● Storø           | ■ Mông Hsu      | ◆ ?Ilakaka    | ■ Tunduru         |
| ◇ Sarfaq         | ● Bjørnesund 2008 | ◆ Pailin          | ● Mogok         | ★ Ilakaka     | ▲ John Saul       |
| × Kangarsuk      | ● Siggartartulik  | ● ?Pailin         | ★ Jagdalek      | ▲ Sahambano   | ● Tsavo           |
| + Tuk            | ▲ Rubin Ø         | ◆ Pailin          | ◆ Jaipur Mysore | ▲ Zazafotsy   |                   |
|                  |                   |                   |                 |               | ● 80% Aappaluttoq |

### 2.3.2 Sapphire

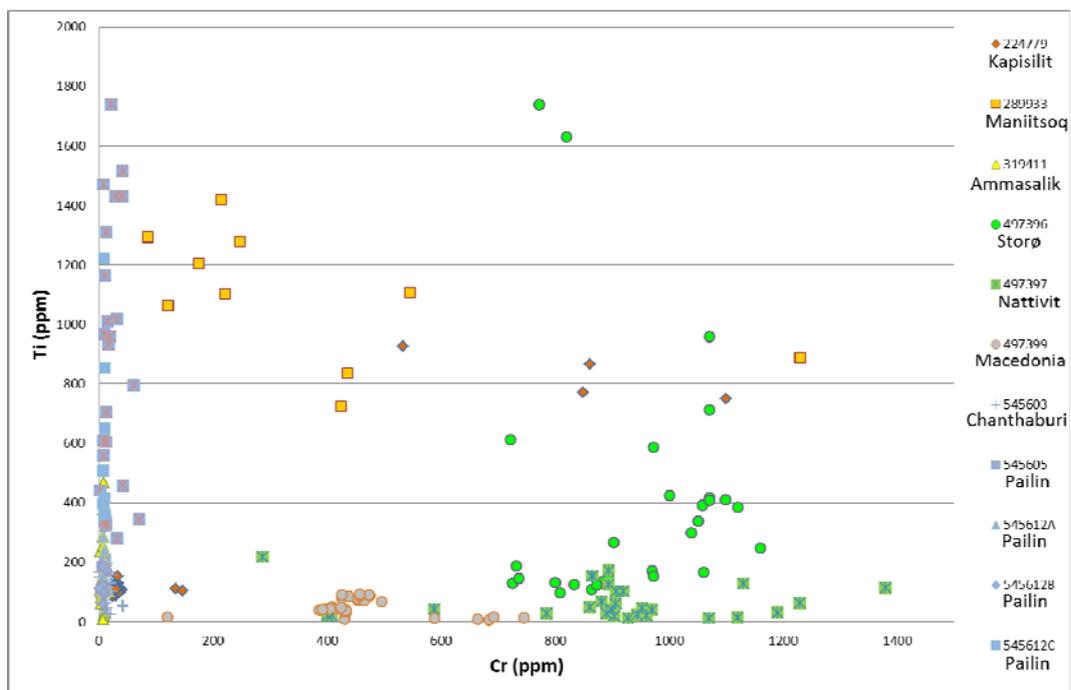
Figure 4 shows the results for the individual analyses on sapphires from Greenland, and from Pailin-Chanthaburi (border region between Cambodia and Thailand) and from Macedonia. The sample from Kapisillit (224779) is characterised by a high contents of Fe (c. 9000 ppm) and V (c. 75 ppm), and a low concentration of Cr, Ti, and Ga. The sample from Maniitsoq (289933) yields high Ti (over 1000 ppm), V (c. 75 ppm), and Mg (c. 150 ppm) concentrations, and a low concentration of Fe and Ga. The sample from Ammassalik (319411) is characterised by a high amount of Fe (c. 9000 ppm), and low concentrations of Cr, V, Ga, and Mg. The sample from Nattivit (497397) shows high relatively high concentrations of Cr (c. 900 ppm), and is low in Fe, Ti, V and Ga. The sample from Storø (497396) is characterised by high Si (c. 1600 ppm), relatively high Cr (c. 900 ppm), and low concentrations of Fe and Ga. The sample from Macedonia (497399) shows low values of many trace elements, especially in Ti, Fe, Ga and Mg. This is also reflected in the rather pale colour of the sample (see Kalvig & Frei 2010). The samples from Pailin-Chanthaburi are characterised by a high amount of Ga (variable, up to 300 ppm), and low concentrations of Cr, V and Mg. The amount of Fe and Ti varies between samples from the region.

From Storø and Maniitsoq, both a sapphire and a pink sample have been analysed. For the samples from Storø, both yielded very similar concentrations of trace elements. The most notable differences are the concentrations of Fe (c. 500 ppm vs. 1500 ppm) and Cr (c. 900 ppm vs. c. 2000 ppm) for the sapphire and the pink sapphire sample respectively. The sample from Macedonia consists of stones with coloured bands that are more reddish or more bluish in colour. Here red-coloured and blue-coloured fragments from the same stones have been analysed. The sample from Maniitsoq shows a wide variability of trace elements within the fragments, even within fragments that to the eye have a near identical colour. This will make samples from Maniitsoq hard to fingerprint.

Most samples from Greenland, and the sample from Macedonia, have been analysed before (Kalvig & Frei 2010). Here, we analysed more fragments per sample to obtain the same data quality as for all other analysed samples. Our results are in concordance with their investigations for many samples, but not for the sample from Ammassalik. Kalvig & Frei (2010) report very high Mg values for this sample (c. 5000 ppm) and describe the sample as an outlier. Our investigations on this sample showed no such high values, even though several pieces from this outcrop were analysed. It is therefore likely that Kalvig & Frei (2010) analysed small inclusions in the sample, possibly spinel.



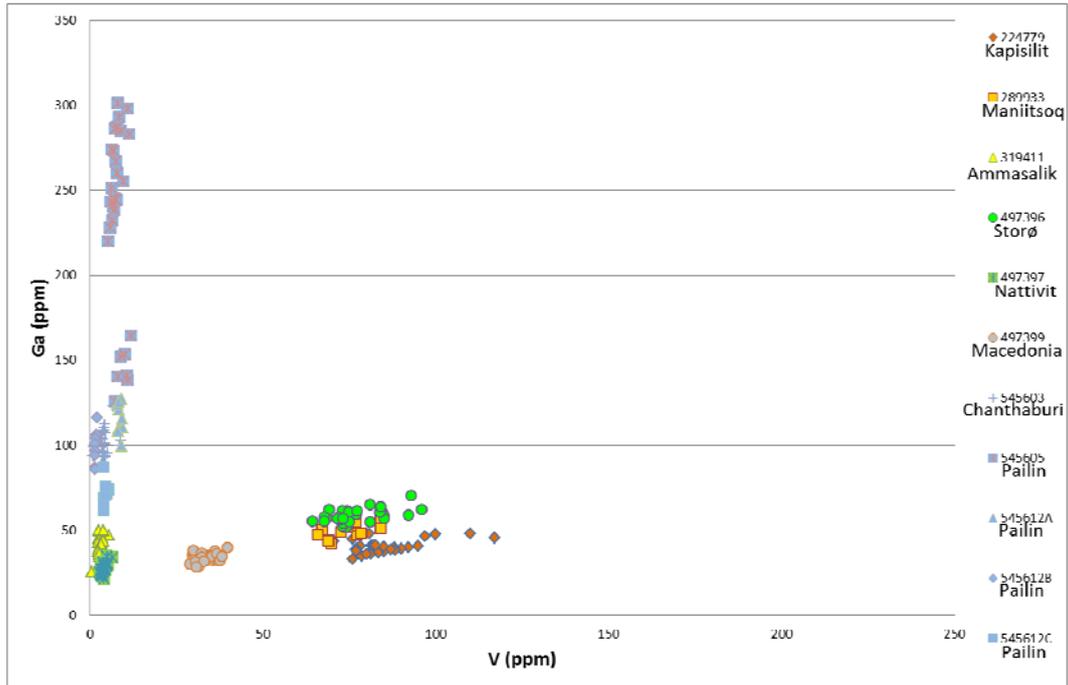
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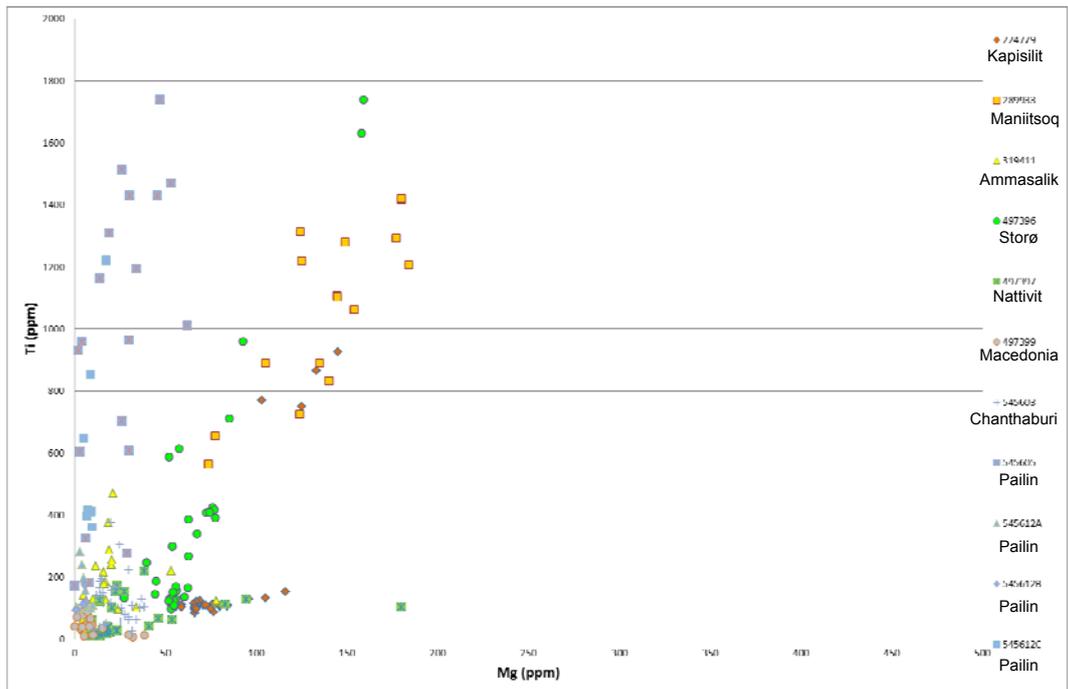
B

Figure 4 (this page and next). LA-ICP-MS data for the analysed sapphire samples; points reflect individual analyses on the samples. **A:** Si vs Fe, **B:** Cr vs Ti, **C:** V vs Ga, **D:** Ti vs Mg.

Figure 4 continued.



C



D

Figure 5 shows the normalised results for the trace elements in sapphire from Greenland and from a few international samples plotted in ternary diagrams. The individual sample regions from Greenland can be separated by the four combinations of trace elements that are shown in Figure 5. The samples can also be separated from the samples collected in Macedonia and in Pailin-Chanthaburi.

However, it is important to realise that many more international occurrences of sapphire exist. In comparison to ruby and pink sapphire, sapphire occurrences are much more abundant. Therefore, the likelihood that the Greenlandic sapphire occurrences overlap in their fingerprint with other international occurrences is great. A comparison with literature data on international occurrences and more testing of sapphire samples would be required to be more conclusive on the Greenlandic sapphire fingerprinting.

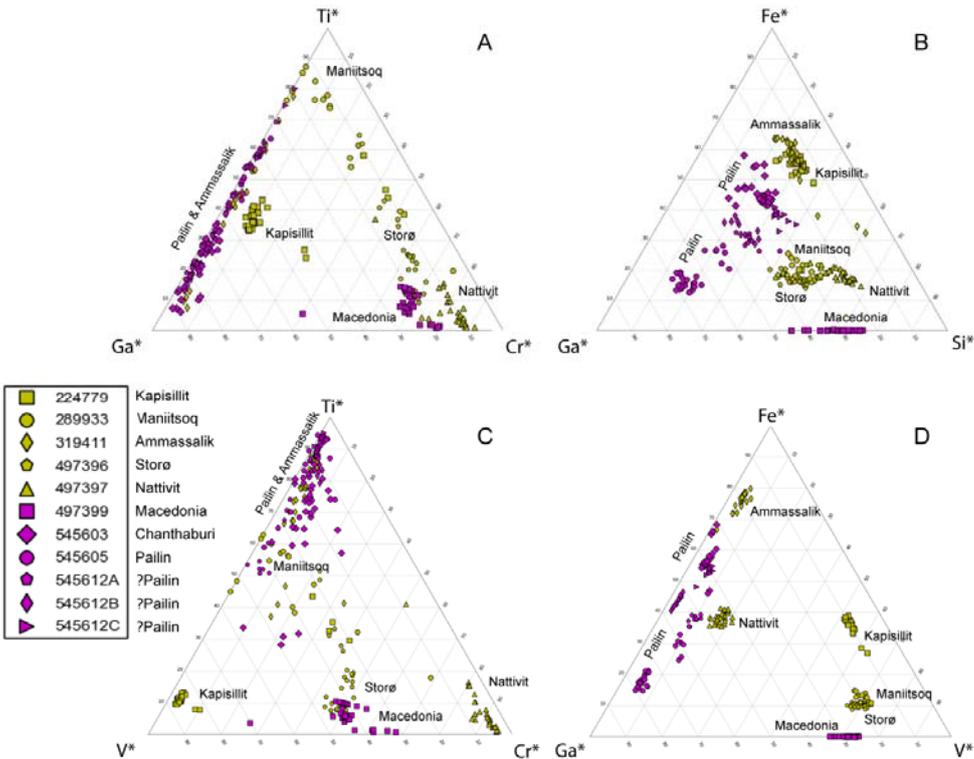


Figure 5. Normalised trace element distributions for Ti-Ga-Cr (A), Fe-Ga-Si (B), Ti-V-Cr (C), and Fe-Ga-V (D) in sapphire from Greenland and from two international occurrences.

## 2.4 Blind test

### 2.4.1 Introduction

Asta F. Jørgensen, MSc-student at Copenhagen University, was given four samples for a blind test. She analysed the samples on the ICP-MS and compared the analytical results with literature data and the GEUS corundum dataset. The four samples were chosen as follows: one sample that was bought at a market in Pailin, Cambodia, (545608-unknown 1) and was claimed to be derived from that area, one from Storø, Godthåbsfjord, (545609-unknown 2), one sample from Aappaluttoq (521111-unknown 3), one from the Fiskenæsset complex, Qaqqatsiaq, (160063-unknown 4).

### 2.4.2 Interpretation of the origin of the samples

The following text is taken from the report made by Asta F. Jørgensen (2014):

In the ternary diagrams the samples are classified by locations and the unknown samples are tried to be tied to a location. Table 2 gives a summary of the information in the ternary diagrams. In the table, the overlapping samples are listed and from that it is tried to give an estimate of where the unknown sample originate from.

*Table 2: Areas, in which the trace element chemistry overlaps with the unknown samples.*

| Name             | FeCrTi                            | FeCrGa                                      | CrTiGa                            | SiFeGa   |
|------------------|-----------------------------------|---|-----------------------------------|--|
| <b>Unknown-1</b> | Pailin<br>Kangarssuk              | Pailin<br>Bjørnsund<br>Aappaluttoq          | Pailin<br>Kangarssuk              | Pailin<br>Bjørnesund<br>Aappaluttoq<br>Beer Mountain |
| <b>Unknown-2</b> | Kangarssuk<br>Pailin<br>Maniitsoq | Kangarssuk<br>Pailin<br>Top 670             | Kangarssuk<br>Pailin              | Kangarssuk<br>Pailin<br>Aappaluttoq                  |
| <b>Unknown-3</b> | Aappaluttoq<br>Rubin Ø<br>Top 670 | Aappaluttoq<br>Pailin<br>Top 670            | Aappaluttoq<br>Top 670<br>Rubin Ø | Aappaluttoq<br>Nattivit<br>Madagascar<br>Pailin      |
| <b>Unknown-4</b> | Aappaluttoq<br>Top670             | Aappaluttoq<br>Qororssuaq East<br>Sri Lanka | Aappaluttoq<br>Sarfaq             | Sri Lanka<br>Tuk<br>Madagascar                       |

**Unknown1** overlaps with Pailin in all four ternary diagrams and with Kangarssuk in Fe-Cr-Ti and in Cr-Ti-Ga, with Aappaluttoq and Bjørnesund in Fe-Cr-Ga and in Si-Fe-Ga, and with Beer Mountain in Si-Fe-Ga. Unknown1 does have most in common with the corundum from Pailin.

**Unknown2** overlaps with Kangarssuk and Cambodia in all four ternary diagrams, in Fe-Cr-Ti there is an overlap with Maniitsoq, in Fe-Cr-Ga Unknown2 overlaps with Top670, and in the Si-Fe-Ga diagram there is an overlap with Aappaluttoq. Unknown 2 is most likely derived from Kangarssuk.

**Unknown3** overlaps with Aappaluttoq in all four diagrams, with Top 670 in all the diagrams except Si-Fe-Ga, with Rubin Ø in Fe-Cr-Ti and Cr-Ti-Ga, with Cambodia in Si-Fe-Ga and Fe-Cr-Ga. An overlap with Nattivit and Madagascar is present in the Si-Fe-Ga diagram. Unknown3 fits best with Aappaluttoq.

**Unknown4** overlaps with Aappaluttoq in Fe-Cr-Ti, Fe-Cr-Ga and Cr-Ti-Ga, with Sri Lanka in Fe-Cr-Ga and Si-Fe-Ga, and with Top 670, Qororssuaq East, Sarfaq, Tuk, and Madagascar in one diagram each. Unknown 4 is hard to fingerprint, but contains the best correlation with Aappaluttoq.

### 2.4.3 Discussion of the blind test

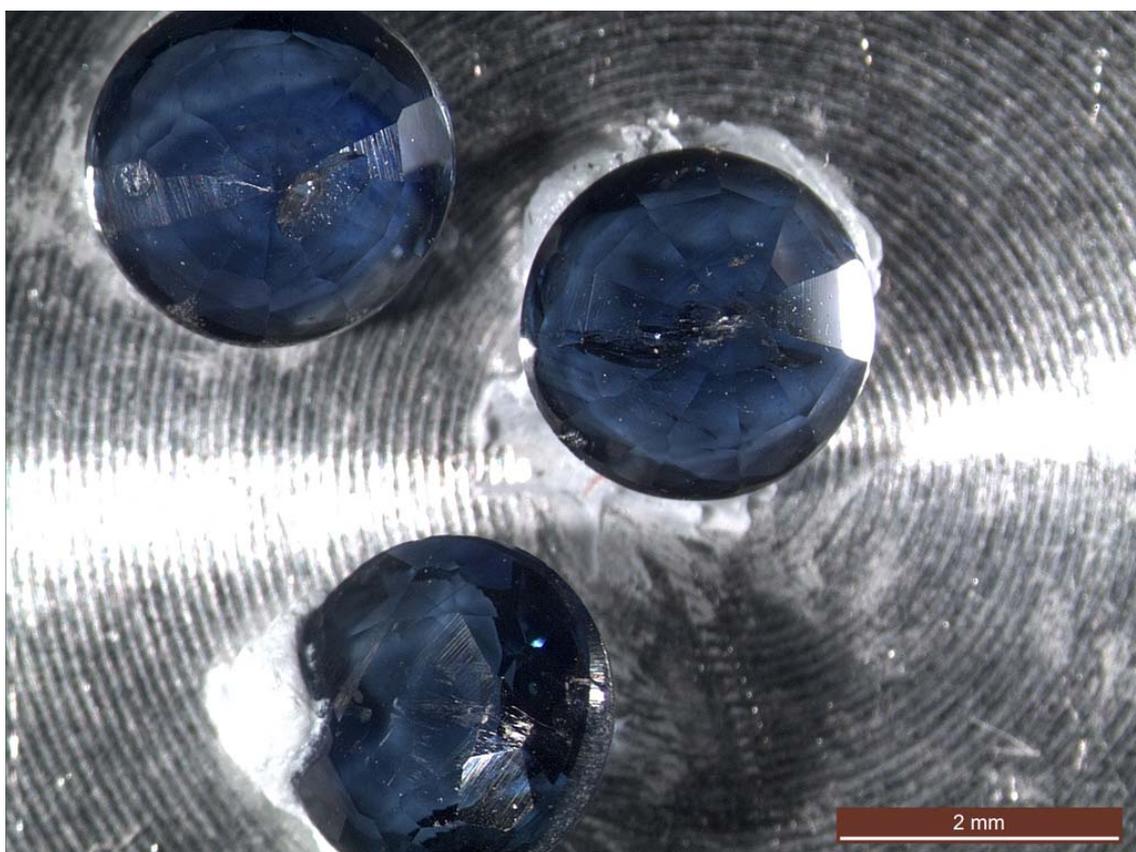
The main aim of the test was to see, whether a sample from Aappaluttoq could be recognised by its geochemical characteristics. The test is skewed, as the Asta F. Jørgensen could reasonably expect that at least one of the samples was from Aappaluttoq, as she was briefly informed about the aim of the ruby project. Furthermore, the GEUS database contains a large set of samples from Aappaluttoq, thus this location is better defined than all other localities. The student only used ternary diagrams for the fingerprinting of the rubies and concentrated her work on only four different ternary diagrams.

Nevertheless, that she was able to recognise a sample from Aappaluttoq as being derived from Aappaluttoq, and a second sample from the Fiskenæsset complex, was also attributed to Aappaluttoq, but with a lesser certainty, and her other options for this sample include many localities within the Fiskenæsset complex. She also recognised the sample from Pailin correctly, even though only a few ruby and pink sapphire samples from this area are contained in the data set.

Unknown 2 was not fingerprinted correctly. This ruby sample from Storø has a large overlap with the sapphire sample from Storø, a fact that was not recognised by the student. This overlap is hard to detect from ternary diagrams that include Fe and Cr, as these two trace elements are not the same for the ruby and sapphire samples. The unknown 2 sample overlapped as well with samples from the Fiskenæsset complex in the Fe-Cr-Ga and Fe-Ga-Si diagrams, but not in Ti-Ga-Cr, Fe-Cr-Ti- and Ti-Cr-V diagrams, and should therefore not be confused with the Fiskenæsset complex.

## 2.5 Effect of ICP-MS analyses on polished stones

Three polished sapphire stones that were bought at the market in Pailin and were claimed to derive from the local area, have been investigated with LA-ICP-MS. The stones are not very well polished, but the images below illustrate the effect of the LA-ICP-MS analyses on the polished stones (Figures 6-9).



*Figure 6. The three analysed polished sapphires seen in an optical microscope. LA-ICP-MS spots in the upper sample were mainly placed in the facets of the culet. In the sample on the right the spots were placed in edges of the facets in the culet, and in the sample at the bottom the spots were placed in the girdle.*

Typical LA-ICP-MS analyses would not be placed on the facets (Figure 7), and certainly not on the facets of the table, as this would influence the way the light is transmitted through the sample, but on the edges of the facets in the culet or in the girdle (Figure 8 and 9). In these samples at least, the marks on the sample left after polishing are larger than the spots burned with the LA-ICP-MS.

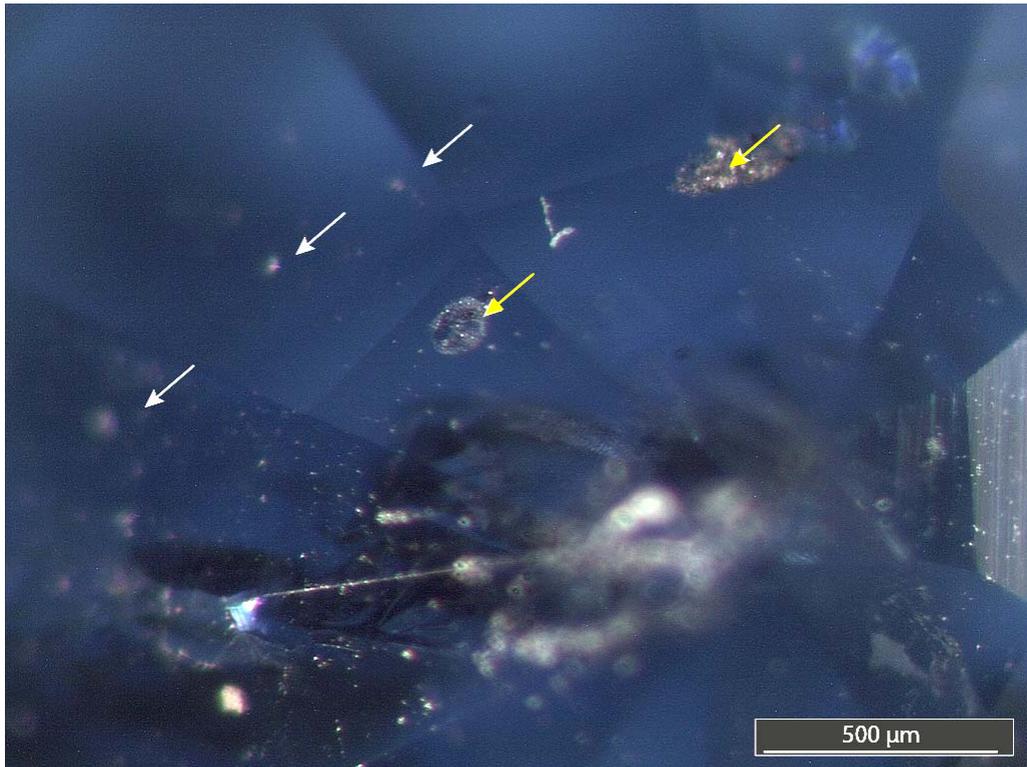


Figure 7. Detail of the upper sample in Figure 6, in which LA-ICP-MS spots mainly were placed in the facets of the culet (white arrows). Damage of the sample inflicted during polishing is shown with yellow arrows.



Figure 8. Detail of the sample on the right in Figure 6, in which LA-ICP-MS spots mainly were placed in the edges of the facets of the culet (white arrows). Damage of the sample inflicted during polishing is shown with a yellow arrow.

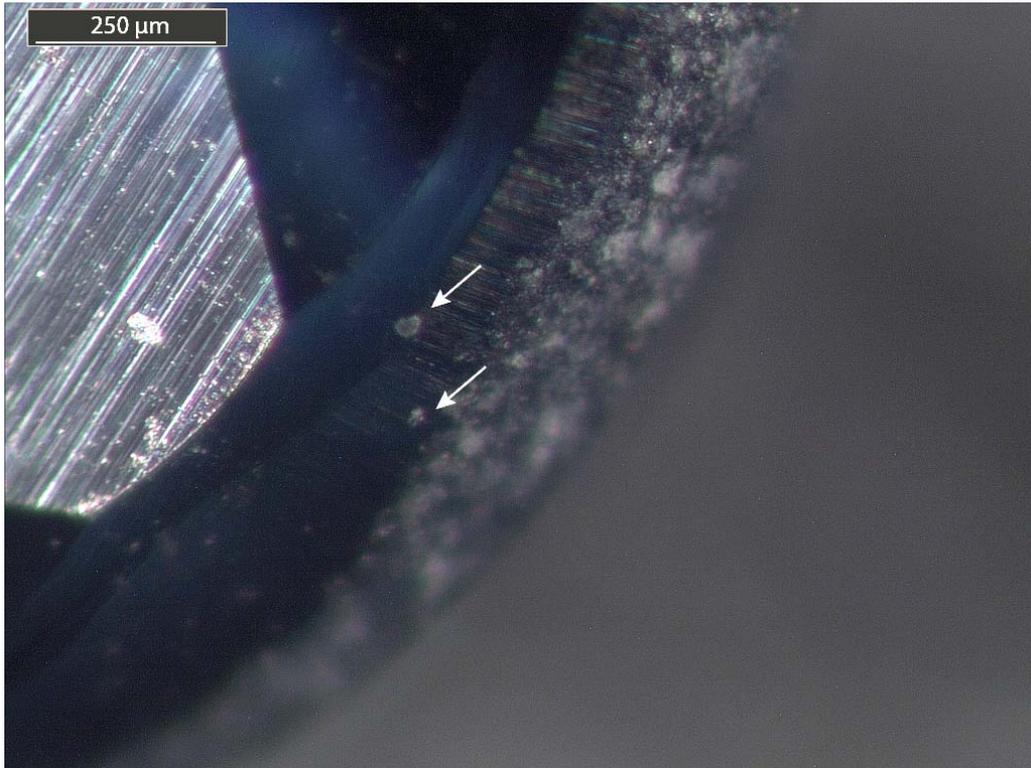


Figure 9. Detail of the lower sample in Figure 6, in which LA-ICP-MS spots mainly were placed in the girdle (white arrows).

## 2.6 Conclusions of the trace element geochemistry investigations

Out of 22 investigated elements, significant results after LA-ICP-MS analyses for Aappaluttoq samples and most other localities were only obtained for Mg, Si, Ti, V, Fe, Cr, and Ga. Samples from Aappaluttoq are enriched in Cr and Fe and low in Ga and Ti compared to international ruby occurrences. Samples from Aappaluttoq can often be differentiated from other localities within the Fiskenæsset complex by their slightly higher Cr contents and lower Fe contents. Those samples are often poorer in inclusions than samples from many other localities within the Fiskenæsset complex. The samples from Aappaluttoq show only minor overlap with samples from other international localities. A preliminary blind test gave good results in the recognition of Aappaluttoq samples. However, more international locations need to be tested for overlap with the Aappaluttoq samples, before the samples from Aappaluttoq can be recognised with large certainty and the results in this study need to be compared to samples of known gemstone quality.

Sapphire samples from Greenland can be separated from each other. They do not overlap significantly in ternary diagrams with other sapphire samples. However, there has not been performed a large international comparison study to be able to separate the Greenlandic samples from international occurrences.

### 3. Raman spectroscopy and fluorescence spectroscopy

Raman and fluorescence spectroscopy analyses were carried out in cooperation with Rolf W. Berg, Department of Chemistry, DTU (Technical University of Denmark).

#### 3.1 Raman spectroscopy

The Raman effect of minerals is based on molecular vibrations in a crystal, which are activated by monochromatic light, e.g. from a laser. The inelastic scattering of the monochromatic light causes a shift in the energy of the laser photons, called a Raman shift. The peaks in the Raman shift spectrum occur at specific values for the studied crystal. Corundum has seven specific phonons (Raman peaks) with bands at 378, 418, 432, 451, 580, 645, and 756  $\text{cm}^{-1}$ . Which peaks occur, depends on the orientation of the crystal with respect to the monochromatic light (Porto & Krishnan, 1967). Hence, usually only three or four of the seven known peaks occur. In case the crystal contains impurities, in the form of trace elements or as tiny mineral inclusions, extra peaks occur in the Raman spectrum. These peaks have been used to characterise rubies and especially (blue) sapphire occurrences.

Analyses were performed with a visible light argon-ion laser with a wavelength of 532 nm on a LABRAM Raman Spectrometer (Horiba Jobin-Yvon, Villeneuve d'Ascq, France).

#### 3.2 Results and discussion of the Raman spectroscopy analyses

Figure 10 shows the results of the Raman spectroscopy investigation on corundum. Two synthetic sapphires were used to calibrate and verify the system. Several of the theoretical Raman bands were observed in these synthetic sapphires.

A ruby crystal from Aappaluttoq (Fiskenæsset) was tested with Raman (GGU #521104). The sample was very fluorescent, causing a large noise peak on the right side of the spectrum. This fluorescence suppressed the Raman bands that are nearly invisible in the spectrum. The high fluorescence is caused by the presence of chromium (Cr) in the sample. Sample 521104 has a moderate amount of Cr, compared to other Aappaluttoq samples, thus even more fluorescence is expected of gem-quality rubies.

To demonstrate the applicability of Raman on natural corundum, a pale blue sapphire crystal from Tanzania has been analysed. The sapphire shows several of the typical Raman bands that indicate corundum, but also gave some extra peaks, which are caused by impurities in the crystal. Further investigations would have been necessary to attribute these extra peaks to specific trace elements or tiny mineral inclusions.

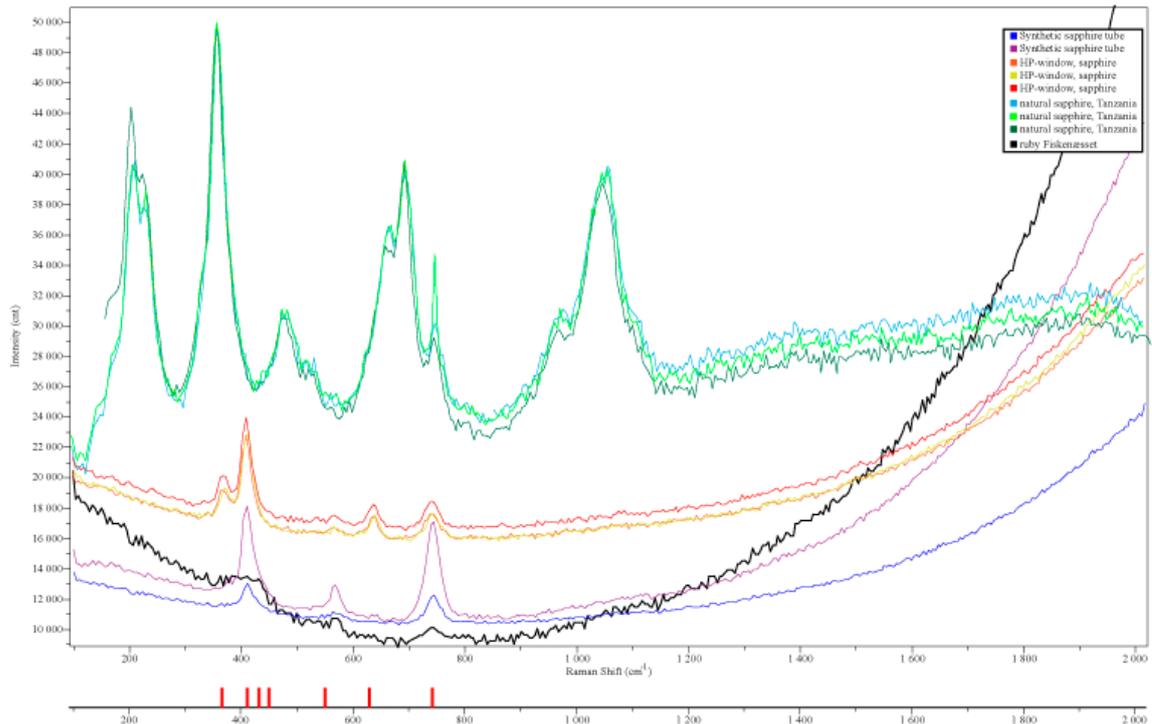


Figure 10. The Raman effect of corundum. Raman shift of two synthetic sapphires, natural (faint blue) sapphire from Tanzania, and Fiskeneset (Aappaluttoq) rubies in the upper part of the figure and known Raman bands for corundum in the bottom of the figure. The intensity of the Raman spectrum on the vertical axis is at a relative scale, spectra have been shifted upward to enable comparison.

Raman spectroscopy is not suitable to fingerprint the rubies from Fiskeneset, because of the high chromium content. For corundum in general, Raman spectroscopy is very difficult, because the obtained peaks and their relative intensity depend on the crystallographic orientation of the crystal. Hence, it is impossible to obtain a unique spectrum for a crystal. Raman could be used though, to characterise the nature of inclusions in ruby in cases where other techniques are not applicable, and to detect glass and lead fillings.

### 3.3 Fluorescence spectroscopy

The fluorescence of a sample depends on the ability of the sample to emit light as a result of an electromagnetic radiation. In the case of these fluorescence spectroscopy investigations, a laser with visible light was used (532 nm). The fluorescence effect is caused by the absorption of photons in the sample, which is exciting the sample, causing molecular vibrations. The sample emits energy again, usually of a lower frequency, which can be measured. The fluorescence of corundum strongly depends on the amount of Cr present in the crystal structure, pure  $\text{Al}_2\text{O}_3$  is non-luminescent and a higher amount of the trace element Fe reduces the fluorescence. Ruby has two typical lines, R1 and R2, which are placed at 692.6 and 694.2 nm at room conditions (see Figure 11).

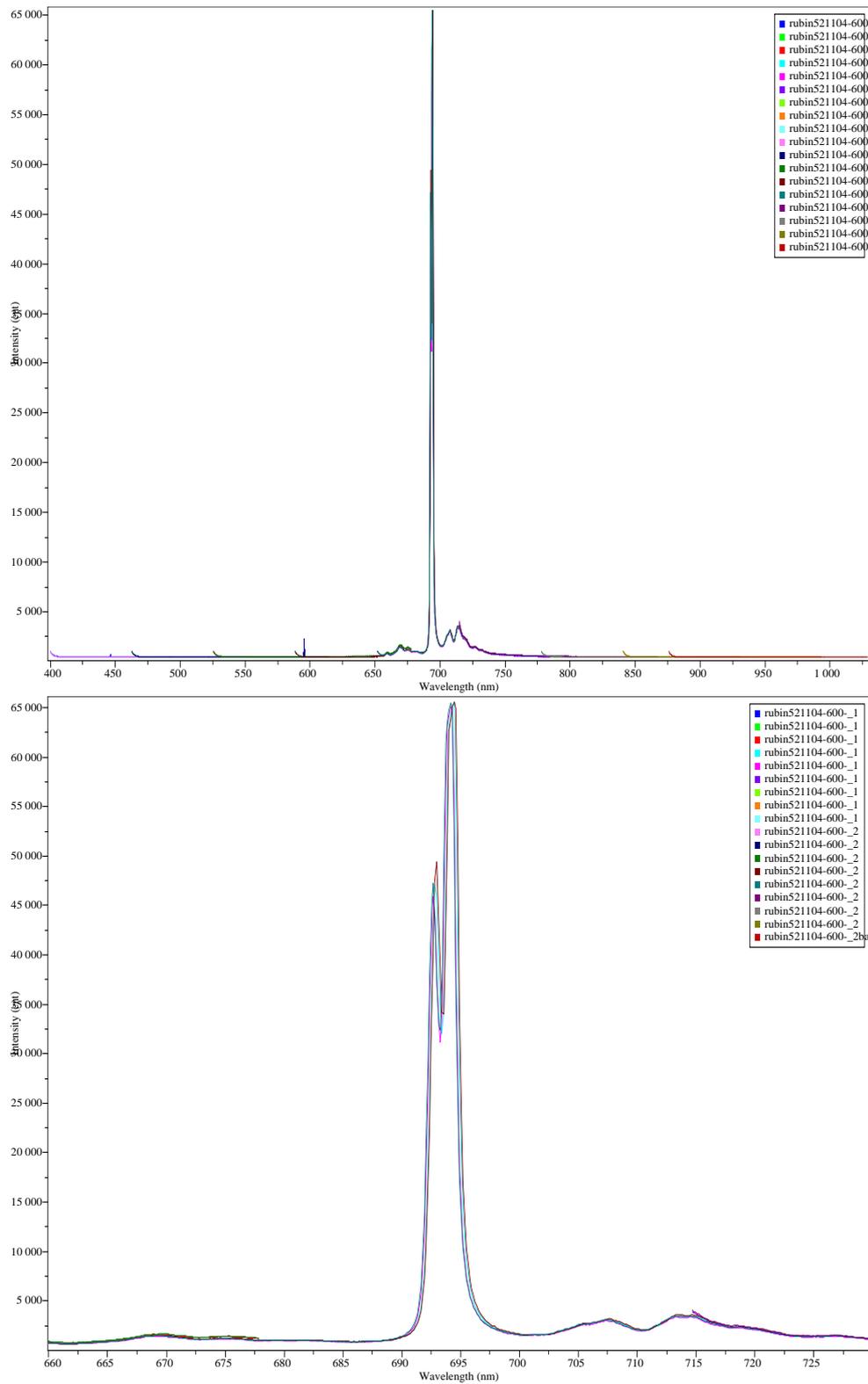


Figure 11. Fluorescence effect of Aappaluttoq ruby (sample 521104). The ruby shows its characteristic peaks at wavelengths 692.6 and 694.2 nm. The figure at the bottom is a blow-up of the large peak in the upper figure.

Analyses were performed with a visible light argon-ion laser with a wavelength of 532 nm on a LABRAM Raman Spectrometer (Horiba Jobin- Yvon, Villeneuve d'Ascq, France).

### **3.4 Results and discussion of the Raman spectroscopy analyses**

The Aappaluttoq rubies show the characteristic R1 and R2 peaks that have been described in literature. Due to the high amount of Cr and low amount of Fe, the samples show a well-developed fluorescence. No special peaks or other features were observed, thus this technique is not suitable for fingerprinting.

## 4. Micro-XRF investigations

### 4.1 Introduction

Ideally fingerprinting is performed with non-destructive methods. In this light the micro-X-ray fluorescence has been tested as a fingerprinting method. The technique can be applied in two ways. Either point analysis can be made to characterise the trace element chemistry of the corundum grains, or a scan of the whole crystal or part of it can be made in order to show all characteristic features of a polished or non-polished stone.

### 4.2 Micro-XRF method

Micro-X-ray fluorescence ( $\mu$ XRF) is an elemental analysis method, which can examine very small sample areas.  $\mu$ XRF uses direct X-ray excitation to induce characteristic X-ray fluorescence radiation from the sample for elemental analysis. Unlike conventional XRF, which has a typical spatial resolution ranging from several hundred micrometres to millimetres, micro-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 analysed. The term “micro” indicates the localized regions of the sample can be analysed into a spatial resolution on the micrometre scale, down to about 10 micrometers.

With the  $\mu$ XRF instrument the elemental compositions of a sample and the related spatial distribution are accessible. The  $\mu$ XRF analytical method can be used to measure all elements in the periodic system between Na-U, and the sample material can be solids, liquids and powder. The spatial resolution is between micrometres to mm scale (Beckhoff *et al.* 2006), while the typical spot size is between 20-300 micrometre, depending on the distance between the sample and the capillary optics.

The  $\mu$ XRF instrument applied in this study is a Bruker M4 Tornado based at the Roskilde University (Figure 12). The M4 Tornado is equipped with a large high-speed stage and supports 2D-analysis of inorganic, organic and liquid samples.



Figure 12. The Bruker M4 Tornado micro-XRF analyser. <http://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/micro-xrf-and-txrf/m4-tornado/overview.html>

The micro-XRF has the advantage of being able to measure high concentrations of elements from ppm to wt% fast and is a non-destructive analytical method. One of the weaknesses with the micro-XRF method is a higher uncertainty when measuring the lightest elements in the periodic table such as O, Si and Mg, which could be eliminated with a synchrotron source beam.

### **4.3 Micro-XRF and LA-ICP-MS analysis of Greenlandic corundum**

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 Greenland. The corundum samples for comparison came from the localities Bjørnesund, Rubin Ø, Kigutilik, Upper Annertusoq and Lower Annertusoq.

The analytical methods  $\mu$ XRF and Laser ablation Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) were used for fingerprinting purposes, in order to test the elemental concentration of the rubies and the quality of the analyses performed with the  $\mu$ XRF compared to LA-ICP-MS.

The LA-ICP-MS method obtains a spatial resolution in micrometre and can measure all elements in the periodic system between Li-U. For the LA-ICP-MS method about 25-30 points were selected for elemental analysis of the corundum. The elements measured by the LA-ICP-MS were Mg, Si, Ti, V, Cr, Fe and Ga. LA-ICP-MS is a method that makes use of standards and known unknowns for the analyses, therefore the accuracy of the measurements can be checked. For the  $\mu$ XRF analysis areas close to points analysed by the LA-ICP-MS were chosen. Five to six points in each sample were analysed. The elements measured by the micro-XRF were O, Mg, Al, Si, Ti, V, Cr, Fe, Ga and Zr. The chemical formula for corundum is  $Al_2O_3$  and some of the elements can substitute into the crystal structure of corundum giving the colour varieties from colourless corundum to ruby, pink corundum and sapphire. The elements Si, Ga, Mg, Fe, Cr, V and Ti can substitute for Al in the corundum. Zr is present in a filter in the  $\mu$ XRF instrument and therefore gives a false-positive signal.  $\mu$ XRF analyses are standard-free analyses.

### **4.4 Results and discussion of the comparison between the micro-XRF and LA-ICP-MS method**

The average of the elemental concentration for the samples from  $\mu$ XRF and LA-ICP-MS analysis were compared, and plotted on diagrams for the elements Mg, Si, Ti, V, Fe, Cr, and Ga (Figure 13 to 19). The LA-ICP-MS can measure very small concentrations of elements in the range ppb to ppm. The spot size for analysis is much smaller than for the  $\mu$ XRF from about 30 micrometer to 100 micrometer. The LA-ICP-MS measures fairly fast, but leaves a tiny hole in the sample after measurements. The LA-ICP-MS has a small spot

size and measures the elemental concentration in the rubies more precisely than  $\mu$ XRF. The method is also better suited for measuring inclusions in the corundum, because the smaller spot size will give a smaller uncertainty for the elemental concentrations.

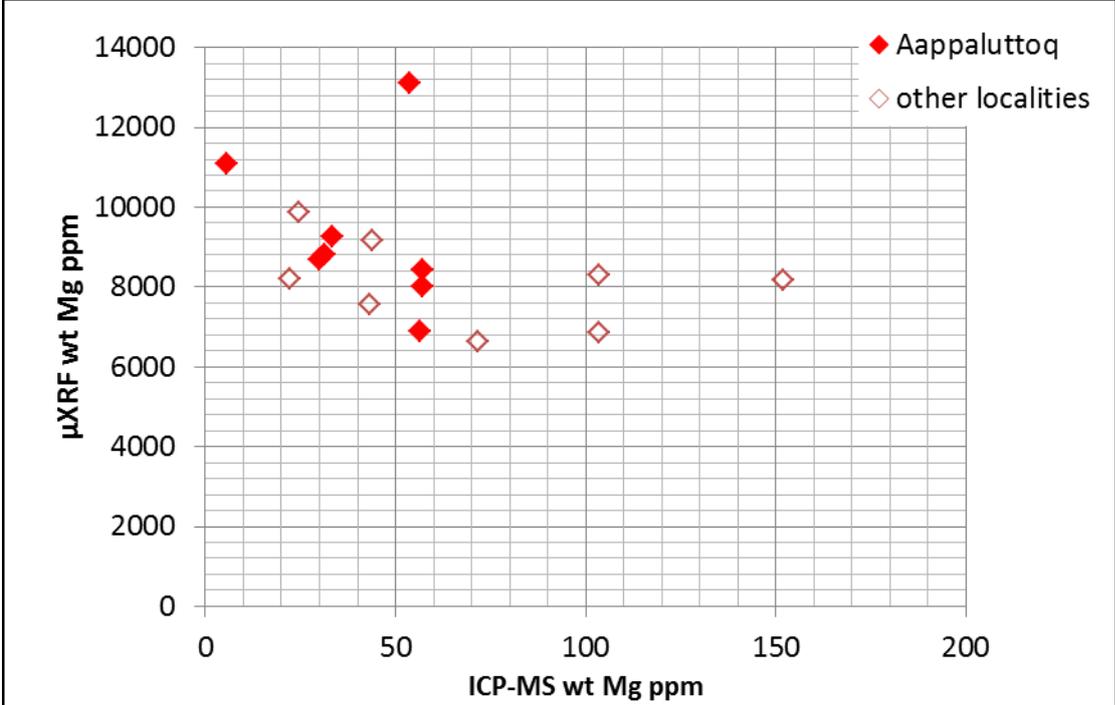


Figure 13. The average of the results for Mg in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland. The Aappaluttoq samples plot with less scatter.

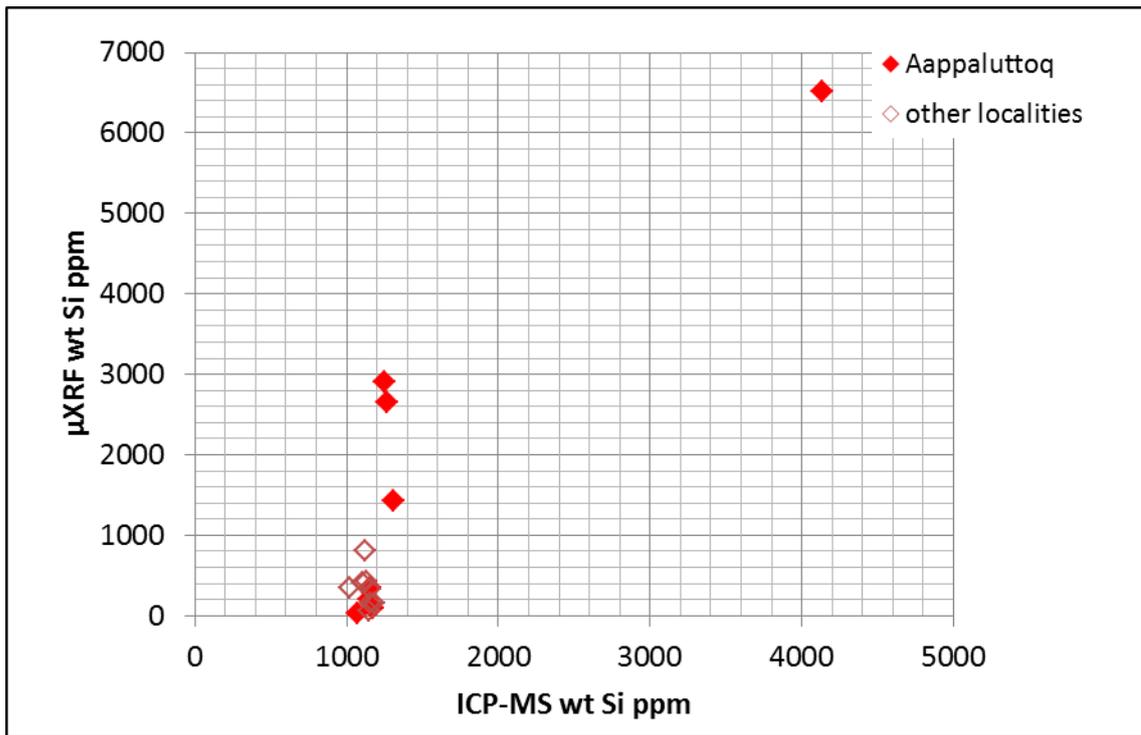


Figure 14. The average of the results for Si in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland. The Aappaluttoq samples plot with less scatter.

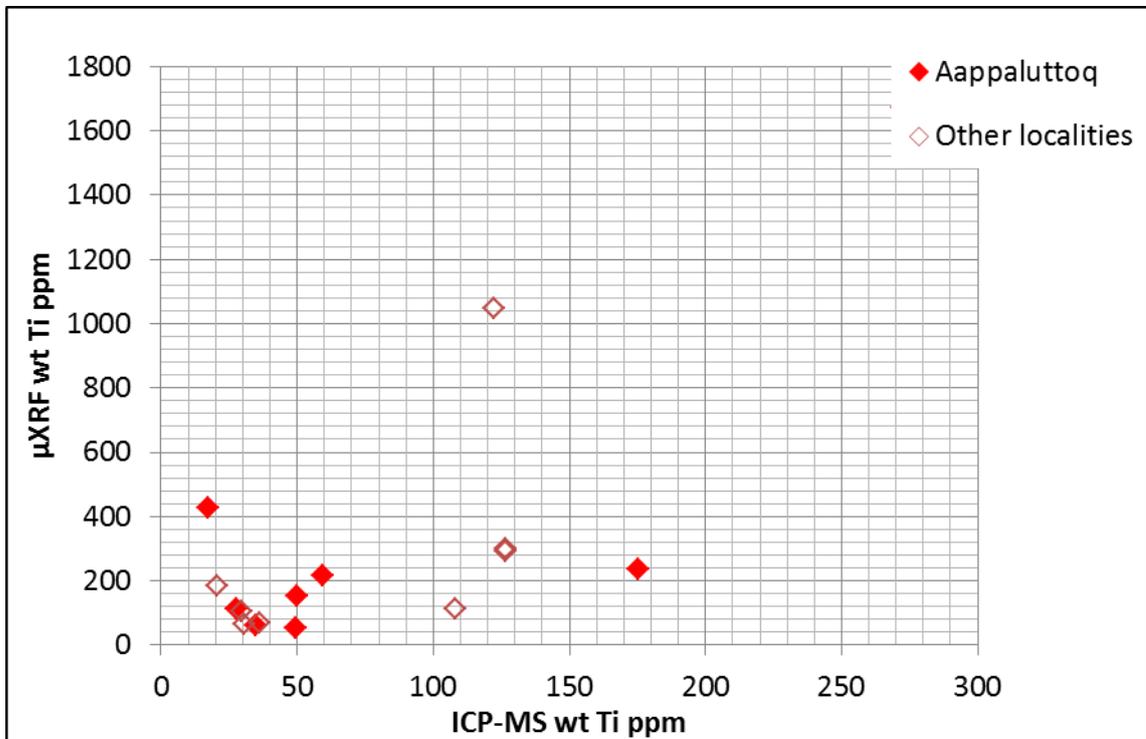


Figure 15. The average of the results for Ti in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland.

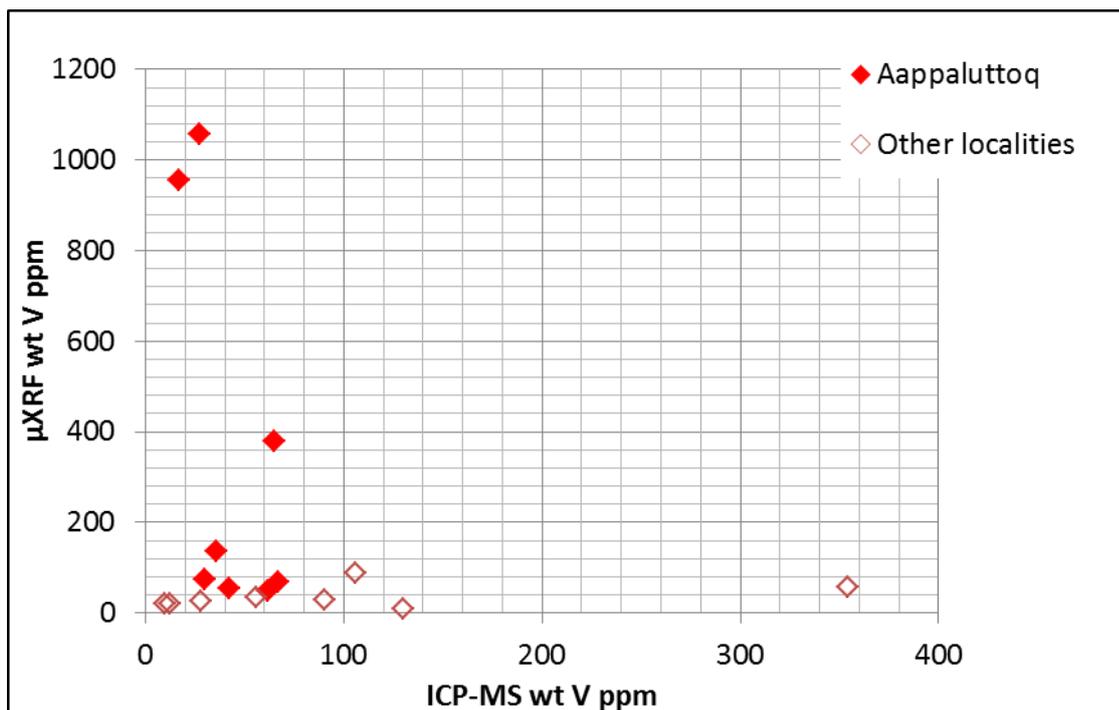


Figure 16. The average of the results for V in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland.

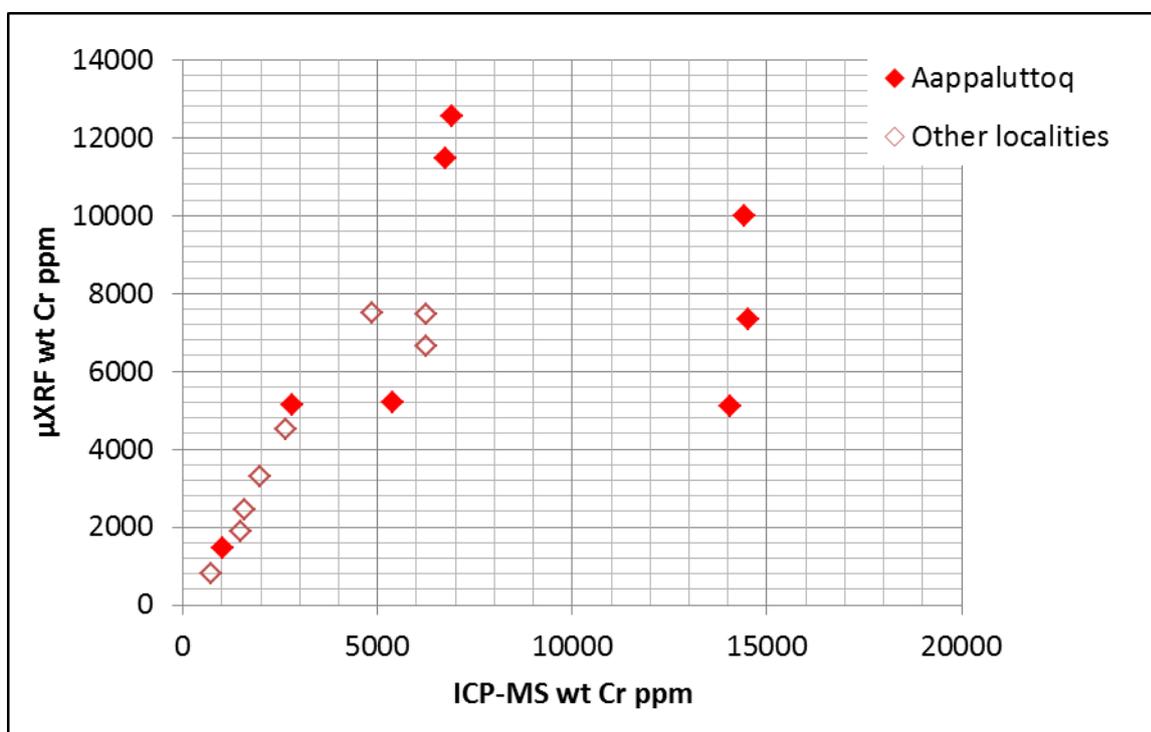


Figure 17. The average of the results for Cr in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland.

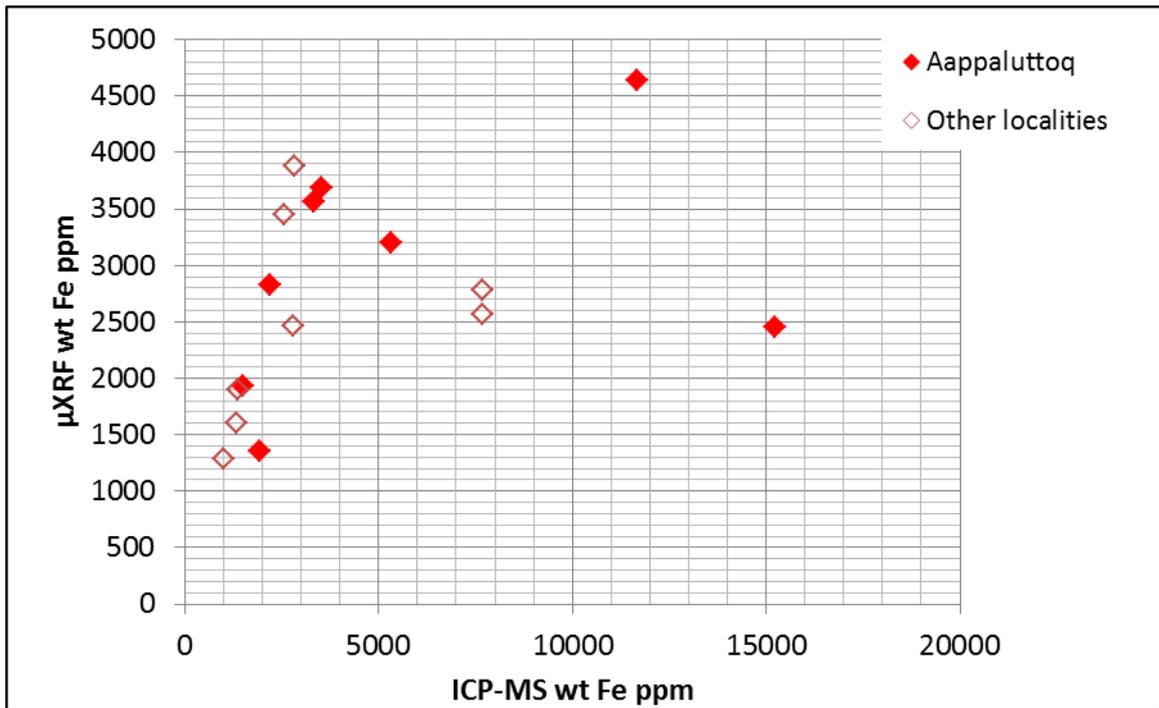


Figure 18. The average of the results for Fe in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland.

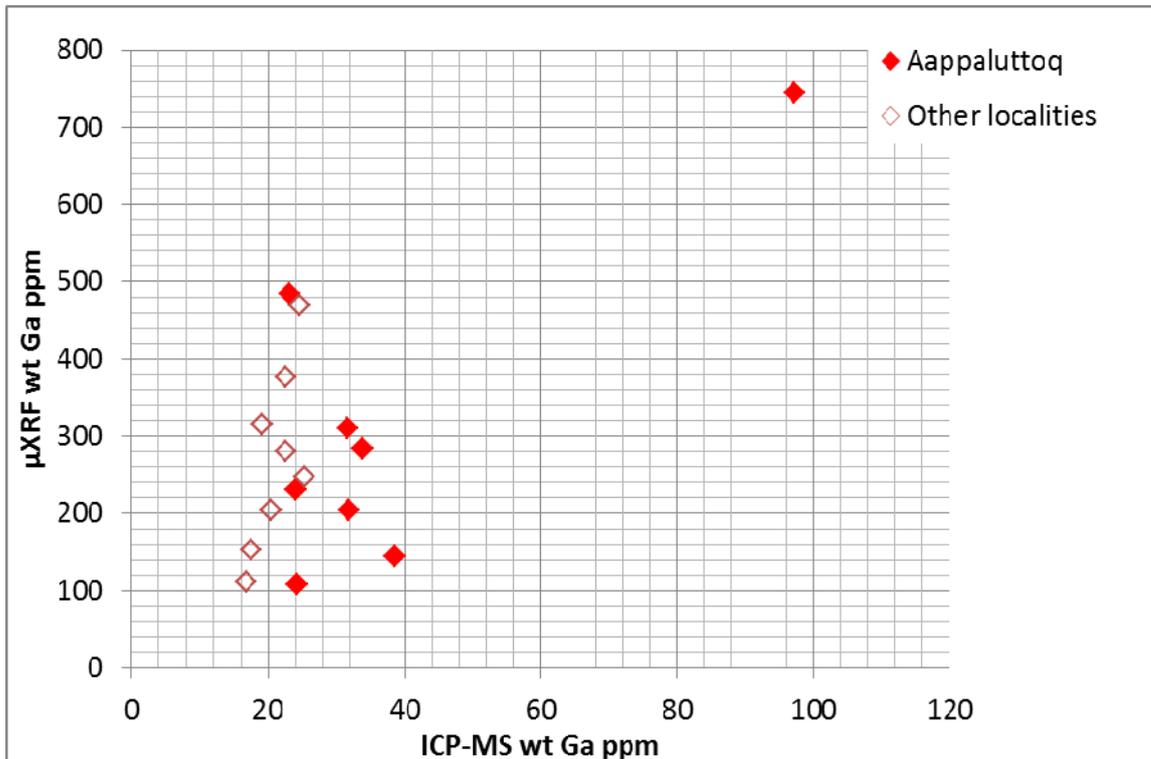


Figure 19. The average of the results for Ga in ppm for the two methods  $\mu$ XRF and LA-ICP-MS. The red diamonds are corundum samples from Aappaluttoq, and the unfilled diamonds are from the other corundum localities in Greenland.

The difference in concentrations for the elements Mg, Si, Ti, V, Cr, Fe and Ga are listed as intervals in Table 3 below.

*Table 3. Comparison between the range in concentration (ppm) for the methods  $\mu$ XRF and LA-ICP-MS. The table shows actual values measured on the same corundum samples from the Fiskenæsset complex.*

| Element | Micro-XRF     | LA-ICP-MS    |
|---------|---------------|--------------|
| Mg      | 6000 to 12000 | 10 to 150    |
| Si      | 100 to 300    | 1000 to 1200 |
| Ti      | 40 to 1600    | 20 to 270    |
| V       | 10 to 350     | 20 to 1100   |
| Cr      | 800 to 14000  | 800 to 12000 |
| Fe      | 1200 to 4600  | 1000 to 5000 |
| Ga      | 100 to 150    | 20 to 40     |

For Mg the concentration between the two methods is more than 100 times higher for the  $\mu$ XRF method, which could indicate that at least one of the methods is not precise enough for the lightest elements (Figure 13). For Si the concentrations measured with  $\mu$ XRF analysis are approximately 1/4 for most of the samples for micro-XRF compared to the LA-ICP-MS analysis (Figure 14). For Ti the concentration measured with micro-XRF is about 4 times larger than with the LA-ICP-MS (Figure 15). For V the concentration for micro-XRF is about 2 times smaller than for the LA-ICP-MS method (Figure 16). The concentration for Cr lies in the same intervals for both methods (Figure 17). The concentrations measured for Fe with the two methods lies within the same intervals, but two samples have higher Fe concentration measured with the LA-ICP-MS method, while most other samples show concentrations that are lower in  $\mu$ XRF than in LA-ICP-MS (Figure 18). For Ga the concentration range measured with the  $\mu$ XRF is about 1/5 of the LA-ICP-MS analysis (Figure 19).

The LA-ICP-MS method has some difficulty when measuring the light elements such as Mg and Si, which can influence the accuracy for the concentrations. However, the difference between the standards and the ICP-MS analyses is small compared to the differences between  $\mu$ XRF and LA-ICP-MS for these elements. When plotting the elements for the methods micro-XRF and LA-ICP-MS there are some differences in the measured concentration of the elements. The differences could be real, because of the points analysed by the two methods are not entirely overlapping, but most likely the differences are due to a too low accuracy of the elemental concentrations for each measurements for at least one of the methods applied.

The difference in results between the two methods is large (Table 4, 5). As the results for the LA-ICP-MS can be compared to the standards and known unknowns that were measured together with the samples, we know that the LA-ICP-MS analyses only have a small error in accuracy and are rather precise. Therefore, the quality of the  $\mu$ XRF analyses is too low to be able to use as a fingerprinting tool. It has been investigated whether a correction factor could be applied to correct the  $\mu$ XRF data. However, the scatter in the  $\mu$ XRF data is too large to be able to do this reliably.

Table 4. Samples of corundum analysed with LA-ICP-MS. The values are the average of 25-30 measurements. The localities are; A =Aappaluttoq, B = U. Annertusoq, C = L. Annertusoq, D= Bjørnesund, E=Kigutilik, F=Intex

| Sample CP-MS average | Locality | Mg_ppm_m25 | Si_ppm_m29 | Ti_ppm_m49 | V_ppm_m51 | Cr_ppm_m52 | Fe_ppm_m57 | Ga_ppm_m71 |
|----------------------|----------|------------|------------|------------|-----------|------------|------------|------------|
| 521108               | A        | 29.92      | 1068.00    | 49.28      | 30.07     | 1035.75    | 15219.33   | 24.33      |
| 521109               | A        | 56.97      | 1173.67    | 272.27     | 16.73     | 2803.00    | 5307.33    | 23.17      |
| 521110               | A        | 57.10      | 1157.67    | 175.37     | 27.53     | 6731.33    | 3332.00    | 31.93      |
| 521111               | A        | 31.30      | 1146.67    | 59.62      | 67.07     | 6905.00    | 1517.37    | 33.96      |
| 521121               | A        | 5.64       | 4134.00    | 17.36      | 35.47     | 5392.70    | 11685.00   | 97.34      |
| 521101               | A        | 33.34      | 1309.66    | 34.90      | 64.82     | 14436.00   | 1932.76    | 31.65      |
| 521105               | A        | 56.58      | 1265.42    | 49.77      | 42.24     | 14511.43   | 3517.08    | 38.60      |
| 521106               | A        | 53.82      | 1246.30    | 27.82      | 61.58     | 14064.00   | 2205.56    | 24.07      |
| 521123               | B        | 71.75      | 1021.33    | 107.96     | 10.27     | 4851.07    | 2569.00    | 16.73      |
| 521127               | B        | 103.34     | 1158.17    | 126.80     | 19.30     | 6239.66    | 7681.38    | 22.68      |
| 521127               | B        | 103.34     | 1158.17    | 126.80     | 19.30     | 6239.66    | 7681.38    | 22.68      |
| 521130               | C        | 43.80      | 1119.33    | 20.65      | 28.11     | 1489.43    | 1364.73    | 20.42      |
| 521131               | D        | 22.29      | 1109.00    | 30.37      | 34.36     | 717.90     | 2831.33    | 24.71      |
| 521132               | D        | 24.70      | 1147.33    | 29.83      | 24.71     | 1569.30    | 2794.00    | 25.39      |
| 521149               | E        | 43.21      | 1130.00    | 36.30      | 56.64     | 2641.34    | 1007.86    | 17.48      |
| 521163               | F        | 151.93     | 1183.69    | 122.10     | 87.69     | 1979.03    | 1343.79    | 19.17      |

Table 5. Samples of corundum with the analytical method micro-XRF. The values are the average of 5 or 6 measurements and are given in ppm. The localities are; A =Aappaluttoq, B = U. Annertusoq, C = L. Annertusoq, D= Bjørnesund, E=Kigutilik, F=Intex

| Sample micro-XRF average | Locality | O         | Mg       | Al        | Si      | Ti      | V       | Cr       | Fe      | Ga     | Zr      |
|--------------------------|----------|-----------|----------|-----------|---------|---------|---------|----------|---------|--------|---------|
| 521108                   | A        | 464574.38 | 8676.06  | 522308.43 | 27.70   | 54.98   | 74.16   | 1459.38  | 2453.68 | 108.06 | 263.18  |
| 521109                   | A        | 461405.64 | 8002.93  | 518745.89 | 89.66   | 1673.55 | 956.79  | 5135.33  | 3197.10 | 484.37 | 308.74  |
| 521110                   | A        | 458683.71 | 8430.61  | 515685.70 | 347.97  | 237.17  | 1056.15 | 11468.59 | 3559.39 | 203.42 | 327.29  |
| 521111                   | A        | 459265.80 | 8812.83  | 516340.13 | 201.85  | 217.77  | 69.07   | 12556.76 | 1927.64 | 284.30 | 323.86  |
| 521121                   | A        | 456599.92 | 11075.20 | 513342.96 | 6511.23 | 426.74  | 135.53  | 5194.53  | 4634.81 | 743.78 | 1335.31 |
| 521101                   | A        | 459845.22 | 9257.70  | 516991.56 | 1425.54 | 61.58   | 379.55  | 9977.99  | 1352.78 | 310.48 | 397.62  |
| 521105                   | A        | 460725.46 | 6887.83  | 517981.18 | 2647.70 | 154.00  | 53.60   | 7338.26  | 3690.80 | 144.35 | 376.84  |
| 521106                   | A        | 459136.58 | 13105.82 | 516194.85 | 2904.88 | 114.09  | 47.84   | 5117.79  | 2830.24 | 230.05 | 317.85  |
| 521123                   | B        | 461865.18 | 6632.88  | 519262.55 | 339.99  | 298.10  | 130.13  | 7513.59  | 3452.65 | 110.58 | 394.35  |
| 521127                   | B        | 461522.53 | 8304.04  | 518877.32 | 149.75  | 293.14  | 12.23   | 7476.80  | 2784.48 | 279.84 | 299.86  |
| 521127                   | B        | 462603.92 | 6851.48  | 520093.10 | 331.21  | 185.26  | 9.92    | 6658.84  | 2563.92 | 375.72 | 326.60  |
| 521130                   | C        | 463971.72 | 9170.69  | 521630.87 | 804.53  | 64.22   | 90.42   | 1892.20  | 1898.12 | 203.97 | 273.25  |
| 521131                   | D        | 464033.12 | 8199.23  | 521699.91 | 405.61  | 104.43  | 56.04   | 807.78   | 3880.31 | 469.23 | 344.33  |
| 521132                   | D        | 463460.96 | 9861.53  | 521056.62 | 67.20   | 69.56   | 27.98   | 2457.21  | 2464.39 | 246.76 | 287.81  |
| 521149                   | E        | 463359.82 | 7569.40  | 520942.94 | 429.45  | 1049.33 | 354.11  | 4515.68  | 1280.84 | 152.80 | 345.64  |
| 521163                   | F        | 464071.25 | 8156.57  | 521742.77 | 160.08  | 241.37  | 106.01  | 3297.61  | 1602.52 | 314.52 | 307.31  |

The second  $\mu$ XRF technique that can be applied on rubies for characterization is the creation of element maps, especially for zones grains and grains with large inclusions (Figure 19). Where tiny inclusions are present in the corundum the spot size is too large to detect these as separate phases. In corundum grains with small inclusions, this will give a high uncertainty for the elemental concentrations of the corundum and the inclusions, as the measurements will be a combination of the elemental concentration of the inclusions and the corundum surrounding the inclusion.

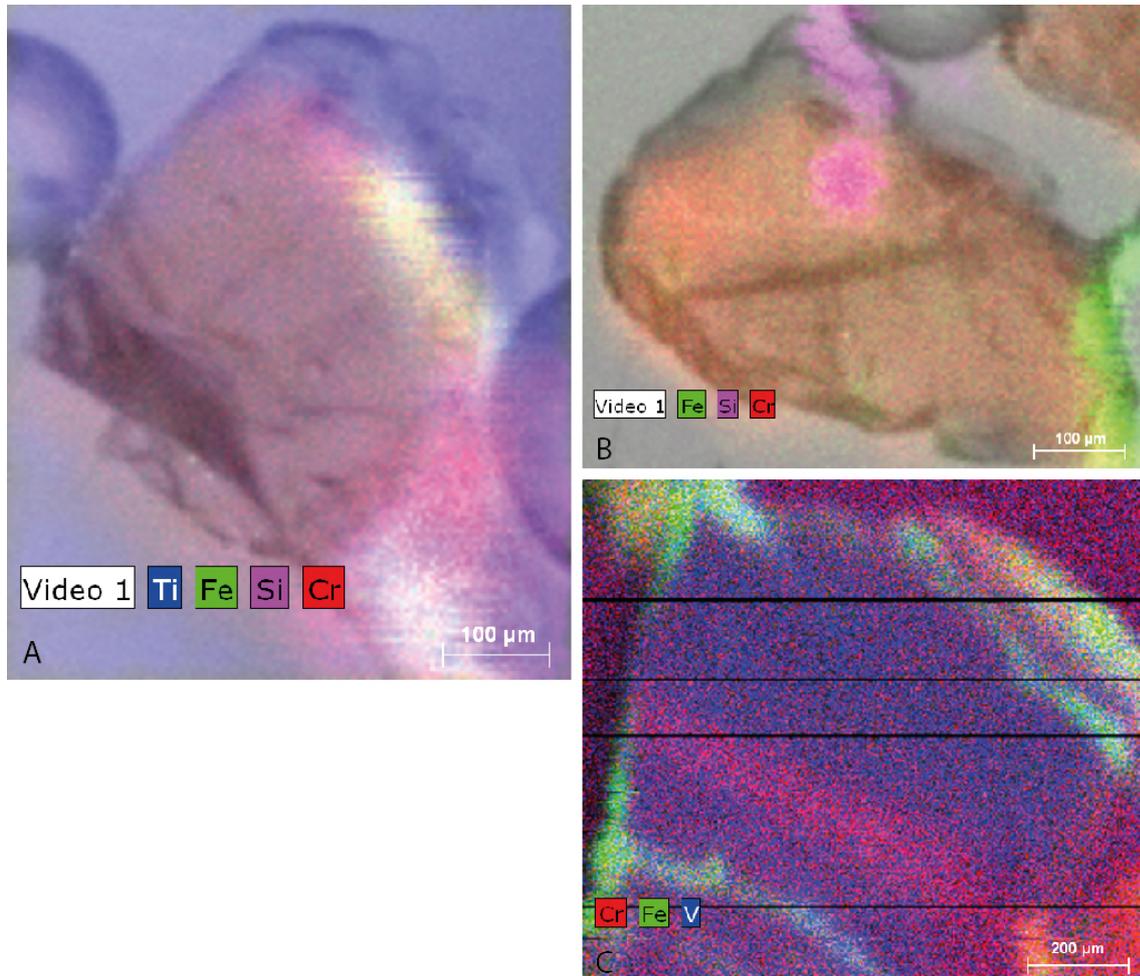


Figure 19. Element mapping with  $\mu$ XRF. A) Corundum grain from Aappaluttoq. B) Corundum grain from Aappaluttoq with an inclusion, possible anorthite. C) Corundum grain from Maniitsoq.

The corundum from the Aappaluttoq area has little chemical zonation in the grains (Figure 19A, 19B), which eliminates the possibility for fingerprinting or crystal characterization by element mapping. The sample from Maniitsoq shows an irregular banding of Cr and Fe in the corundum fragment (Figure C). Other samples also showed zonation in V. If the grains from Aappaluttoq would have been similar to those from Maniitsoq, element mapping as a way to characterize individual stones might have been possible.

## 4.5 Conclusions

1.  $\mu$ XRF, as LA-ICP-MS, indicates that the Aappaluttoq corundum have a higher Cr concentration than most samples of corundum from other areas in the Fischenæsset complex. However, this fact alone is not sufficient to recognise samples from Aappaluttoq with  $\mu$ XRF.
2. Both methods have fairly similar concentrations in Fe and Cr, but these two elements are not sufficient for fingerprinting of the corundum from Aappaluttoq area. Results for Mg, Si, Fe, Ti, V, and Ga are too uncertain to be able to use  $\mu$ XRF as a fingerprinting tool.
3. Element mapping of the trace elements of corundum does not work as fingerprinting method, as the samples from Aappaluttoq are nearly unzoned in trace elements at the detection levels for the  $\mu$ XRF.

## 5. Oxygen isotope analyses

As this report gives the main results from the analyses 2011-2013, we repeat here the most important results of the oxygen isotope investigations that were performed in 2011. No new data is added here. An overview of the results, in comparison with international results for ruby samples is given in Figure 20.

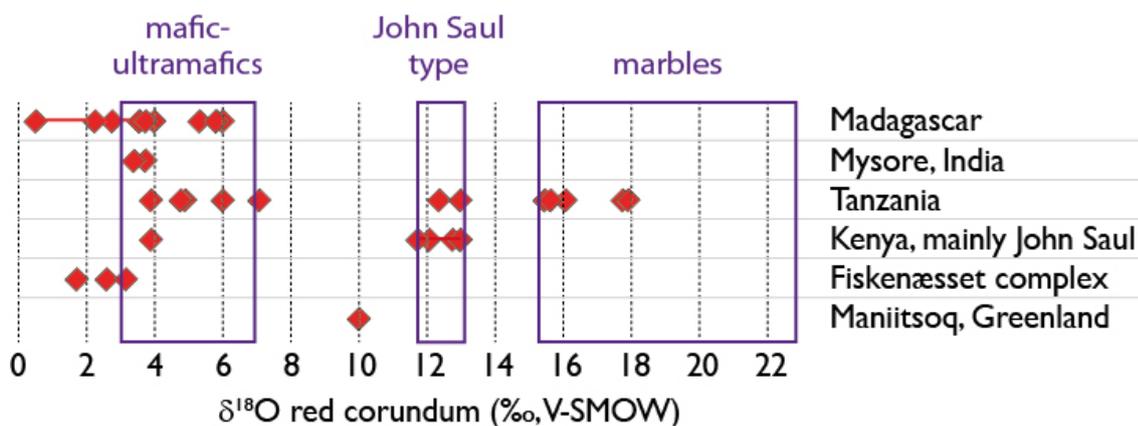


Figure 20. Results from oxygen isotope analyses for red corundum from Madagascar, India, Tanzania, Kenya, Fiskenæsset and Maniitsoq. Data from the non-Greenlandic occurrences and the division into three types of corundum are taken from Giuliani et al. (2005).

The investigated gem-corundum sampled in the Fiskenæsset complex have oxygen isotope ratios that largely overlap with the mafic-ultramafic values reported by Giuliani et al. (2007). This is in good agreement with the general thoughts that the gem-corundum in the Fiskenæsset area is derived from a metamorphic reaction involving the anorthosite and ultramafic rocks in the Fiskenæsset complex (e.g. Schumacher et al. 2011) and by the mineral parageneses, containing pargasite, gedrite, and/or phlogopite with sapphirine, plagioclase, spinel, and/or cordierite and mineral inclusions in the corundum grains.

Oxygen isotope ratios are a helpful parameter to characterise the gem-corundum sampled in the Fiskenæsset complex. Measurements however, need to be combined with other methods to obtain a good fingerprinting of the minerals. The  $\delta^{18}\text{O}$  values vary between 1.62 and 4.20‰ for the Fiskenæsset complex, this lowers the previously reported range of  $\delta^{18}\text{O}$  values (3 - 7‰) for mafic-ultramafic rocks. The ratio for  $\delta^{18}\text{O}$  of the Fiskenæsset samples is lower than in most mafic-ultramafic-derived red corundum grains, but there is a significant overlap with corundum from Madagascar.

The ratio for  $\delta^{18}\text{O}$  of 10.03‰ in the sample from Maniitsoq is typically related to skarns in marble, and to biotitite in gneiss related to a shear zone with high fluid activity (Giuliani et al. 2007). The corundum in Maniitsoq however, is supposed to have formed in a hornblendite. Hornblendites are a rock type that typically would fall in the category mafic-ultramafic rocks. However, the sample from Maniitsoq had the highest  $\delta^{18}\text{O}$  ratio of the analysed samples from Greenland (including the sapphire grains, Keulen & Kalvig 2011). Therefore, it might be that the hornblendite near Maniitsoq was formed in a shear zone with high fluid activity, like the biotitites in Madagascar.

## 6. Conclusions

Samples from Aappaluttoq are characterised by a relatively high Cr and Fe concentration and low concentrations of Ga and Ti. Rubies from the Fiskenæsset complex can be differentiated from other Greenlandic ruby occurrences based on the values for trace elements Fe, Cr, V, Ti, Ga and Si. It seems to be possible to separate rubies from Fiskenæsset from many other international deposits based on trace elements.

Typical inclusions are: spinel, chromite, biotite, amphiboles, rutile, sapphirine, anorthite. Verifications for gem stone quality rubies, where much less inclusions are expected, are necessary to check whether the trace element ratios in gem-quality stones are significantly different.

For a good fingerprinting more analytical parameters ought to be added. Therefore, the possibilities that Raman and FTIR spectroscopy and micro-X-ray fluorescence offer have been evaluated. However, none of these methods provides high quality data that would add to the fingerprinting of Aappaluttoq corundum.

Oxygen isotope investigations, in combination with other methods, are a helpful, yet destructive method to fingerprint rubies.

Other methods that are worth investigating in the future are:

- Optical microscope observations and physical parameters (mineral characteristics)
- UVvis spectrometry (crystallography)
- Laser-induced breakdown spectroscopy (LIBS)

None of the successful methods investigated so far is completely none-destructive; hence it is worthwhile to try these other methods as well.

For a good fingerprinting of the Greenlandic rubies, it is necessary to build up a database with all available analytical information on rubies from Greenland and elsewhere. It is not only necessary to be able to characterise the Greenlandic rubies, but also to know the characteristics of rubies from other localities worldwide that the Greenlandic rubies may need to be compared with.

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