DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2013/9

Report on the activities in the ruby project 2012

A joint project with the Bureau of Minerals and Petroleum

Nynke Keulen & Per Kalvig

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 Bureau of Minerals and Petroleum in Nuuk, Greenland and the Geological Survey of Denmark and Greenland (GEUS), Copenhagen, Denmark. The investigations are mainly aimed at the characterisation of the Fiskenæsset complex rubies, because the most promising ruby outcrop in that area, Aappaluttoq, is likely to be mined in the nearest future by the Canadian company True North Gems (TNG). In the second year of the project on Greenlandic rubies the activities concentrated on the analytical investigation of the rubies collected in the Fiskenæsset complex in the summer of 2011 and on the presentation of the Greenlandic ruby occurrence to the interested public.

In the summer of 2011 Per Kalvig (GEUS), Henrik Stendal (BMP) and Anette Clausen (BMP) collected circa 50 rock samples from 8 localities in the Fiskenæsset complex with the aim to characterise the Fiskenæsset complex ruby occurrences using the gemmological, geochemical and optical investigations (see Kalvig & Keulen, 2011).

From the collected material 32 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). 20 of the samples and 2 other samples (one from Walton's showing (Qaqqatsiaq) and one form southeast of the Bjørnesund near TNGs Qororssuaq locality hence called Qororssuaq East) have been investigated with the Energy Dispersive X-ray Spectrometers (EDX) of the Scanning Electron Microscope (SEM) at GEUS with the aim to chemically characterise the mineralogy of the inclusions in the rubies and with laser ablation sector-field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) at GEUS in order to investigate the trace element distribution. These investigations will be reported in Chapters 2 and 3 respectively.

Ruby samples from the Fiskenæsset complex are generally rich in mineral inclusions and a whole suite of different minerals has been observed. The samples from Aappalutoq, however, 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. Other mineral inclusions cannot be used to characterise the Fiskenæsset complex very well, but are important clues in the understanding of the metamorphic processes that formed the rubies. A good comprehension of these processes might enable us to predict where to search for further occurrences of rubies or sapphires.

Trace element investigations with a LA-ICP-MS instrument appears to be a promising tool in the fingerprinting of the Greenlandic ruby. Based on the trace elements (Mg,) Si, Ti, (V), Cr, Fe, and Ga for the highest quality samples from Aappalutoq, 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 the same for low and high quality stones.

We performed some preliminary Raman Spectroscopy analyses at the DTU, which are reported in Chapter 4. Analyses were performed to characterise the Greenlandic rubies with a non-destructive method. The preliminary conclusion of these investigations is that Raman spectrometry does 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. However, more work on Raman and other types of spectroscopy will be performed in 2013.

On the 12th-13th December, Nynke Keulen (GEUS), participated in "The 3rd International Gem and Jewlry Conference" in Bangkok, Thailand. The conference and associated excursion were organised by the Thailand public organisation the Gem and Jewelry Institute of Thailand (GIT). The excursion on the 14th – 16th December visited Chanthaburi (Eastern Thailand) and Pailin (Cambodja). From BMP Thomas Lauridsen and Lærke Louise Thomsen participated. Before the conference, two jewelry sellers were visited in Bangkok. During the conference and excursion, three cutting facilities, a heat treatment facility and three small scale miners were visited. These visits, information obtained during our stay in Thailand and the abstracts of the conference oral presentations were summarised in a separate note (to be released by BMP). A copy of the PowerPoint presentation and the extended abstract by Nynke Keulen & Per Kalvig, with the title: "Oxygen isotopes and geochemical characteristics of corundum (ruby) from Fiskenæsset, Greenland – identification and origin determination" are included in the appendices to this report.

The initial findings for the characteristics of the Fiskenæsset complex will be published by Nynke Keulen and Per Kalvig in the Review of the Surveys Activities under the title: "Identification and origin determination of corundum (ruby) from Fiskenæsset, Greenland". This article is expected to be published later 2013. The draft version of the text is appended to this report.

This report refers to corundum, pink sapphire and ruby as rubies irrespective of the quality of the stone or the intensity of the red colour.

Contents

2. Inclusions in ruby and their correlation with colour and transparency

2.1 Energy dispersive X-ray spectrometry (EDX)

Inclusions in the rubies were studied at GEUS using a Philips XL40 Scanning Electron Microscope (SEM) equipped with two EDX detectors: a Thermo Nanotrace 30 mm^2 window and a Pioneer Voyager 2.7 10 mm^2 window Si(Li) detector. Ruby and sapphire grains were crushed to small pieces, mounted in epoxy, polished and coated with carbon. Inclusions are visible as different shades of grey with a back scattered electron (BSE) detector. Approximately 30 pieces per sample were investigated. The tungsten filament of the SEM was operated with an acceleration voltage of 17 kV, a filament current of typically 50–70 µA, and the sample was placed at a distance of 10 mm from the detector. The Noran System SIX software package was used to collect X-ray spectra of inclusions in the ruby and to recalculate the data following the Proza (φρZ) data correction and the filtering quantification technique. Data is provided as wt% oxides.

EDX analysis is a grain surface technique; therefore stones with a high amount of inclusions were selected to study the inclusions in the rubies and sapphire. Mineral classification is based on EDX data alone, no further detailed petrography was undertaken to classify the inclusions. In cases of overlapping chemistry, the most likely mineral classification is applied. For example: TiO_2 is the chemical formula for rutile, brookite and anatase. Rutile however, is the most likely mineral inclusion in rubies, as it is a high-temperature metamorphic mineral, which brookite and anatase are not.

2.2 Inclusion mineralogy

Within the rubies from the Fiskenæsset complex, a range of inclusions has been observed. The most common inclusions are spinel/gahnite, chromite, rutile, biotite, gedrite, anthophyllite, pargasite, sapphirine and anorthite (see Table 1). A few grains of zircon, baddeleyite, ilmenite, andesine, muscovite, calcite, dolomite, pyrite (Fe_xS_y), alumnosilicate, cordierite, brucite/periclase and clay minerals have been found as well.

Table 1 (next page): Observed inclusions in rubies from the Fiskenæsset complex. The mineralogy is compared to the transparency, colour, size and abundance (within a hand specimen) of the Fiskenæsset samples.

sample	508132	508660	521101	521104	521105	521106	521108	521109	521110	521111	521121	521123	521127	521130	521131	521132	521138	521140	521142	521149	521163
	Qororssuaq East	Qaqqatsiaq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	U. Annertusoq	U. Annertusoq	L. Annertusoq	Bjørnesund 2008	Bjørnesund 2008	Siggartartulik	Siggartartulik	Rubin Ø	Kigutilik	Intex
anorthite/andesine	x							x	x	x	x	x	x	x	x	x	x	x			x
zircon/baddeleyite	x		x												x					x	
ilmenite/rutile	x	x		x							x	x	x		x			x		x	
biotite/stilpnomelane		x	x		x	x	x	x		x				x	x	x	x	x	x		
muscovite											x									x	
pargasite				x					x												
anthophyllite/gedrite/amphibole	x	x	x		x						x		x								
cordierite		x		x							x		x								x
spinel/chromite/gahnite			x		x			x	x			x	x						x	x	
sapphirine/alumnosilicate			x		x						x		x						x	x	
calcite/dolomite								x			x										
FexSy/pyrite		x																		x	
brucite/periclase		x		x					x												
kaolinite/Ca-Na-clay/clinochlore	x	x							x					x				x		x	

sample	508132	508660	521101	521104	521105	521106	521108	521109	521110	521111	521121	521123	521127	521130	521131	521132	521138	521140	521142	521149	521163
	Qororssuaq East	Qaqqatsiaq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	Aappaluttoq	U. Annertusoq	U. Annertusoq	L. Annertusoq	Bjørnesund 2008	Bjørnesund 2008	Siggartartulik	Siggartartulik	Rubin Ø	Kigutilik	Intex
ilmenite/rutile	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
biotite/stilpnomelane	x	x	x	x	x			x	x	x	x	x	x	x	x	x	x	x	x	x	x
muscovite	x	x	x	x	x			x	x		x	x	x	x	x			x	x	x	
pargasite	x	x	x	x	x			x	x		x		x		x			x		x	
anthophyllite/gedrite/amphibole	x	x	x						x		x		x							x	
cordierite		x									x		x							x	
spinel/chromite/gahnite		x									x									x	
sapphirine/alumnosilicate																					
calcite/dolomite																					
anorthite/andesine																					
zircon/baddeleyite																					
FexSy/pyrite																					
brucite/periclase																					
kaolinite/Ca-Na-clay/clinochlore																					
Inclusions	2	2	1	1	1	1	1	1	1	1	2	1	2	2	1	1	2	1	1	2	1
Transparency	3	3	5	1	5	4	1	1	3	5	3	1	1	2.5	2.5	5	1	4	4	2	3
Colour			8	1	8	8	3	11	12	8	6	6	8	2	6	11	1	10	5	9	7
Size	1	1	1	3	1	1	3	3	3	1	3	3	1	1	1	2	3	1	1	2	1
Abundance	2	2	2	5	3	3	5	5	5	2	5	5	3	2	4	4	5	5	2	3	2
Quality (Transparency + Colour)			8.5	1.5	8.5	7.5	2.5	6	8.5	8.5	5.5	3.5	4.5	3.5	5	10	1.5	8.5	6	6	6
Concentration (Size + Abundance)	3	3	6	6	4	6	8	8	5	6	8	6	3	5	5	7	8	3	4	4	1

Mineral inclusions
3 Few
2 Medium
1 Plenty

Transparency
5 Good
4 Some Good
3 Medium
2 Low
1 Milky

Colour
12 Medium dark red, very slightly brownish
11 Medium dark, slightly purplish red
10 Medium dark, slightly purplish red, very slightly brownish
9 Medium dark, slightly purplish red, slightly brownish
8 Medium dark, strongly purplish red
7 Medium dark strongly purplish red, very slightly brownish
6 Medium dark strongly purplish red, slightly brownish
5 Medium dark, reddish purple
3 Light red, very slightly brownish
2 Light strongly purplish red, very slightly brownish
1 Light reddish purple

Size
3 Big
2 Medium
1 Small

Abundance
5 Plenty
4 Rather Plentiful
3 Rather few
2 Few
1 Very few

Most samples have either biotite or rutile inclusions, and three samples have both. Pargasite and anthophyllite and/or gedrite are often found in combination with inclusions of Al-rich minerals like sapphirine, cordierite, spinel/gahnite. The inclusion mineralogy is not constant for a certain locality, nor do typical series of mineral inclusion occur on several localities. Only the combination biotite+anorthite was observed three times on three different localities.

As the Fiskenæsset complex is one of very few or maybe the only location in the world where rubies are formed out of anorthosite, the presence of anorthite inclusions is a typical characteristic of the Greenlandic rubies. However, anorthite inclusions are not found in every single ruby grain.

Many of the inclusion minerals are also observed in the hand specimen. In the latter, ruby, ±anorthite, ±sapphirine, are observed in a matrix of either biotite, gedrite/anthophyllite, pargasite, or a combination of these minerals (see also Schumacher et al., 2011; Ritchie, 2006). As for the inclusion mineralogy, there is not a single mineralogical paragenesis for a single locality. Individual localities are characterised by a range of mineral parageneses, a certain grain size, the presence/absence and mineralogy of reaction rims around the rubies and the amount and kind of accessory phases.

A direct correlation between the inclusion mineralogy and the most abundant minerals within the hand specimen has not been observed. Samples with a biotite matrix sometimes show gedrite inclusions and vice versa. However, since the inclusion mineralogy and the hand specimen mineralogy of the localities shows the same mineralogy, it may be assumed that the rubies were formed during the last major metamorphic event in the Fiskenæsset area.

2.3 Correlation with colour and transparency of ruby

Table 1 shows a numerical classification of the transparency of the rubies from milky to good. From the SEM observations, the amount of inclusions in the rubies is estimated as low (1), medium (2) or high (3). There is a weak correlation between the amount of observed mineral inclusions and the transparency of the ruby (Figure 1A). The transparency is dependent on the total amount of inclusions, including fluid inclusions, while the SEM only sees the inclusions in the polished surface of the studied grains.

There is a very weak correlation between the transparency of the grains and the mineralogy of the inclusions (see Table 1). Rubies with a good transparency have often no rutile inclusions, but shows some biotite flakes.

There is no correlation between the colour of the rubies and their inclusion mineralogy. A weak correlation however exists, between the colour of the rubies and their size + abundance in the hand specimen (see Figure 1B). Samples with small and few rubies have a slightly darker red colour. This is tentatively attributed to a high diffusion coefficient for Cr in silicates, for equal Cr-concentrations in the rock. In other words, it seems that the available amount of Cr is distributed over the ruby grains in the vicinity. If only few or small ruby grains are available, their colour will get more intensely red. However, the major factor influencing the colour remains the amount of Cr available in the rock, which is highest closest to the ultramafic rocks.

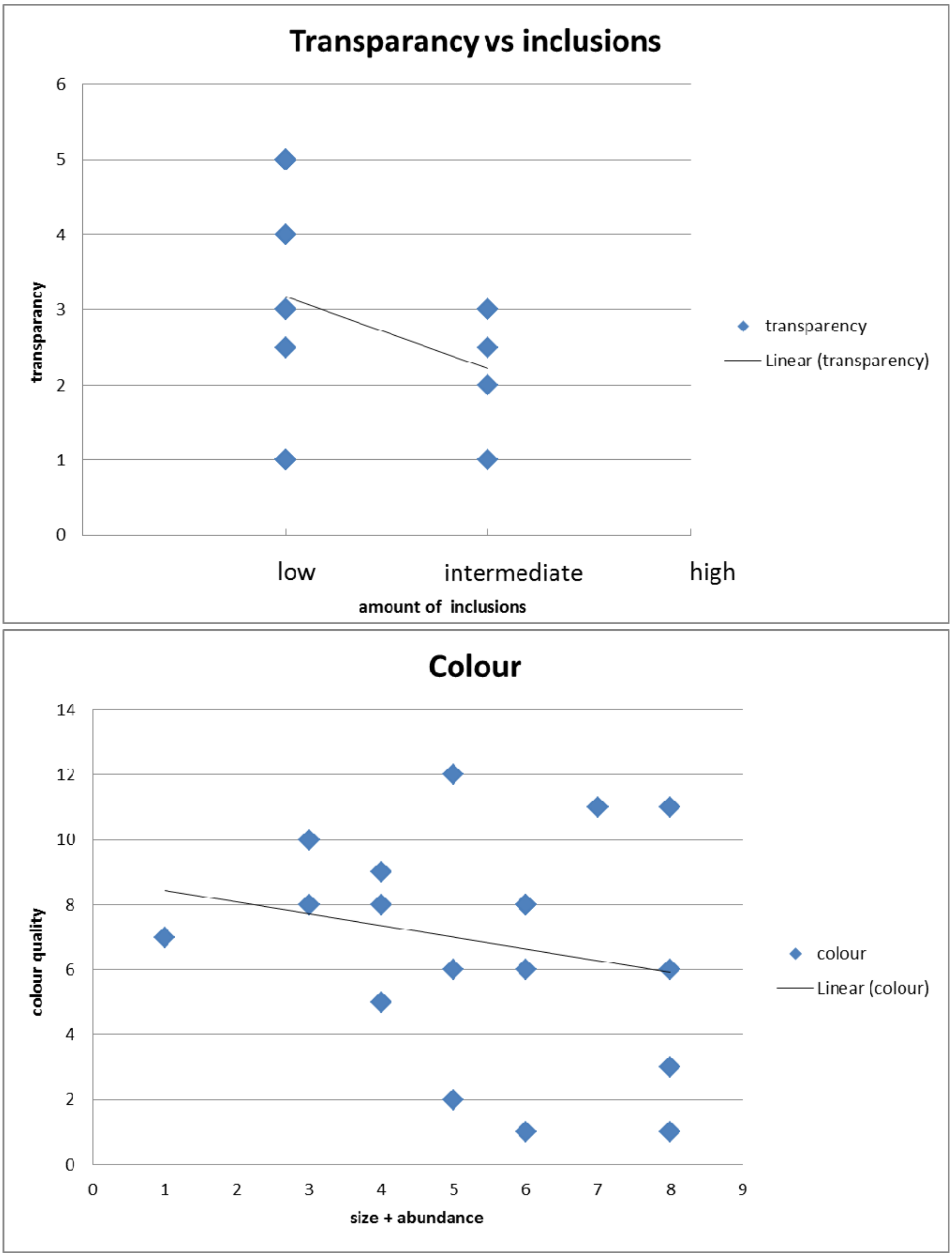


Figure 1. A (top): Relative amount of inclusions correlated with the transparency of the rubies. B (bottom): Size and abundance (within the hand specimen) of the rubies compared to their colour quality. Numbers in both graphs correspond with the values given in Table 1 and are an expression for relative quantities.

3. Trace element geochemistry as a tool for finger-printing rubies

3.1 Introduction

Ruby has the chemical formula Al_2O_3 and like most other minerals usually includes very small quantities of other elements in its crystal structure. The amount of these trace elements and their ratios depend on the geological conditions during the formation of the ruby and vary therefore between individual ruby deposits. The concentrations of 24 different elements were measured with laser ablation-ICP-MS, however most investigated elements were not detected in the rubies. Trace element geochemistry investigations on the Greenlandic ruby 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.

3.2 Methods

Trace element concentrations of 24 elements in ruby from Fiskenæsset were determined on mineral separates by isotopic analyses using laser ablation sector-field inductively coupled plasma mass spectrometry (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 listed in Table 2.

To ensure stable laser output energy, a laser warm-up time of min. 15 minutes were applied before operation, providing stable laser power and flat craters by a “resonator-flat” laser beam. The mass spectrometer was run for at least one hour prior to analyses to stabilize the background signal. Samples and standards were carefully cleaned with ethanol before loading to remove surface contamination. After sample insertion the ablation cell was purged with the helium carrier gas for a minimum of 15 minutes to minimize gas blank level. The helium was blended with argon make-up gas ca. 0.5 m before introduction into the plasma.

Table 2 (next page): Laser ablation sector field inductively coupled plasma mass spectrometry operation and data acquisition parameters.

Table 2. LA-SF-ICP-MS operating and data acquisition parameters

Laser system	**New Wave Research UP213 solid state Nd:YAG laser with aperture imaging**
Laser wavelength	213 nm (Nd:YAG)
Laser mode	Q-switched (Nd:YAG)
Nominal pulse width	4 ns (Nd:YAG)
Repetition rate	10 Hz
Spot sizes (diameter)	25 µm
Energy density on sample	10 J/cm^2 (homogenized energy distribution)
Ablation cell	Small, two-volume cell
Ablation cell gas flow rates	380 ml/min He
Tubing for gas flow	Tygon S-50 HL (5 mm i.d.)
Laser beam focus	Fixed at sample surface

ICP-MS	**Thermo-Fisher Scientific ELEMENT 2 double-focusing sector-field ICP-MS**
Interface cones	Ni sampler and skimmer cone
Detector type	single-collector discrete dynode electron multiplier
Detector mode	cross-calibrated pulse counting and analogue
Detector vacuum	10^{-7} mbar (during analysis)
Argon gas flow rates (l/min):	
Plasma	16
Auxiliary	0.90
Sample	0.955
RF power	1110 W
Lenses (V):	
Extraction	-2000
Focus	-870
X-Deflection	3.00
Y-Deflection	-3.40
Shape	109
SEM potential	2315 V

Data acquisition and processing	
Isotopes measured (sampling times in ms in brackets)	^{11}B (10), ^{25}Mg (25), ^{27}Al (5), ^{29}Si (15), ^{49}Ti (25), ^{51}V (25), ^{52}Cr (25), ^{55}Mn (10), ^{57}Fe (25), ^{64}Zn (10), ^{65}Cu (25), ^{71}Ga (30), ^{72}Ge (10), ^{88}Sr (15), ^{90}Zr (10), ^{93}Nb (10), ^{98}Mo (10), ^{120}Sn (10), ^{133}Cs (10), ^{137}Ba (10), ^{139}La (15), ^{140}Ce (15), ^{178}Hf (15), ^{181}Ta (15), ^{208}Pb (10)
Settling times	1 ms; 7-33 ms at magnet jumping (10 jumps)
Dead time	25 ns
Integration window	10 % except Ga (60 %) and V, Cr, Mn, Fe, Cu, Zn, Mo, Sn, Cs and Ba (80 %)
Samples per peak	1
Aquisition mode	Time resolved analysis
Scan type	E-scan
Detection mode	Both
Integration type	Average
Mass resolution	300 (low)
Oxide production rate	Tuned to ≤ 0.7% UO_2 ($^{254}UO_2/^{238}U$)
Analysis duration	30 s. blank, 30 s. ablation and 20 s. washout.
Software for data reduction	Iolite vers. 2.2 (Hellstrom et al. 2008)
External standardization	BCR-2 and NIST-612 glasses
Internal standard isotope	^{27}Al

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}Ti to ^{208}SPb) with simultaneous opting for low element-oxide production levels by minimising the $^{254}UO_2/^{238}U$ ratios. Instrumental drift was minimized 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 2σ accuracies of <16%, except for Mg (10-40%, depending on the concentration).

Data were acquired from single spot analysis of 25 μm, using a pulse rate of 10 Hz and a nominal laser fluence of ~10 J/cm2. Total acquisition time for single analyses were ~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).

3.3 Results and Discussion

Analyses for the Fiskenæsset complex rubies were performed on 20 different elements. Only Mg, Si, Ti, V, Cr, Fe, and Ga gave significant results. The elements B, Mn, Zn, Cu, Ge, Sr, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Hf, Ta, and Pb are not present in significant amounts in the Fiskenæsset rubies. The Mg-concentration lies close to the detection limit of the ICP-MS system and these data therefore have a lower accuracy. Data for the trace elements are relatively consistent for the various samples from the Fiskenæsset complex for Fe, Mg, Si, Ti and Ga (Figure 2). For a single sample (510132-Qororssuaq East) Ti is high and this might be the result of small (nano-scale) rutile needles that are present as inclusions in the sample. However, Cr varies widely and is closely related to the colour of the minerals, as well as. V varies even within samples from a single outcrop and might be a result of zonations in the individual minerals.

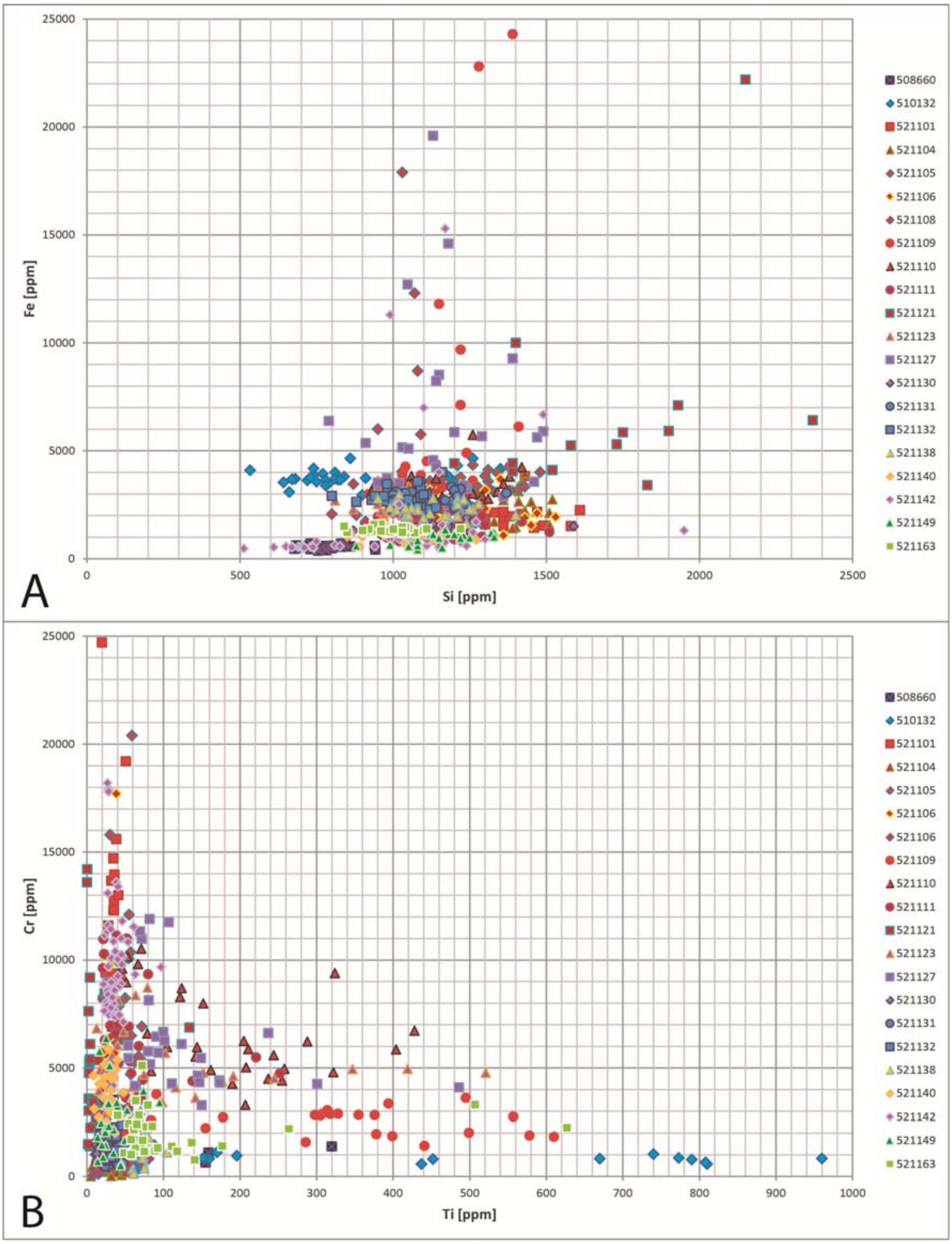
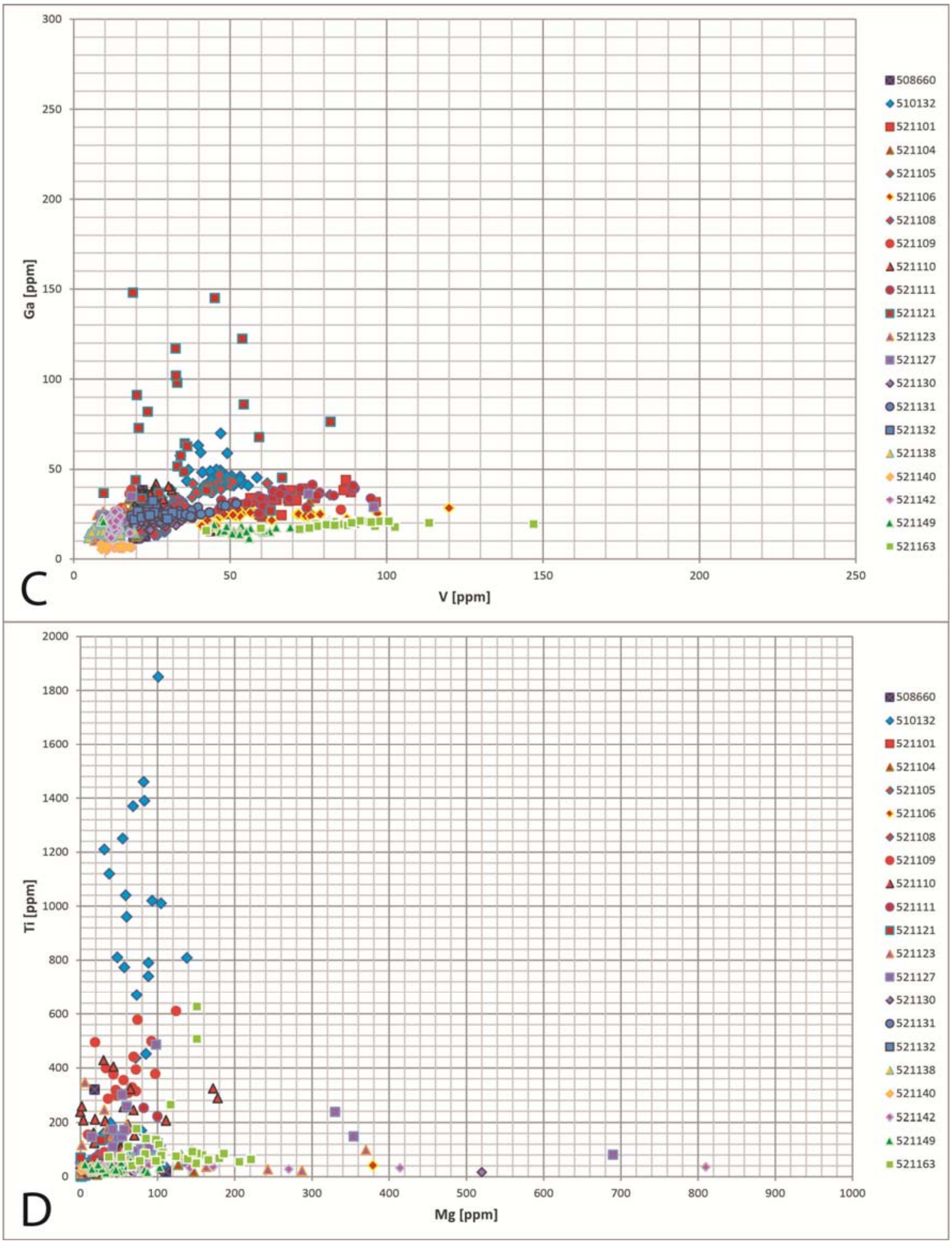


Figure 2 (this page and next): LA-ICP-MS data for samples from the Fiskenæsset complex. Each colour represents a different outcrop in the Fiskenæsset complex, see Table 1 for sample localities. ***A****: Fe vs Si,* ***B****: Cr vs Ti,* ***C****: Ga vs V,* ***D****: Ti vs Mg.*



Results on the trace element investigations for 21 samples representing 10 localities in the Fiskenæsset Complex are shown in ternary diagrams in Figure 3 in red. The data for ruby from the Fiskenæsset Complex are in good concordance with earlier data from Kalvig & Frei (2010) and Thirangoon (2008) for that area. The samples are compared to other samples from Greenland and to samples from internationally, well-known, ruby occurences (see Figure 3). Samples from Fiskenæsset show a considerably higher amount of Cr than samples from other areas in Greenland and most international samples. The Fiskenæsset complex rubies are relatively rich in Fe and Si, but relatively poor in Ti and Ga, while V and

Mg do not show very distinctive values compared to samples from other areas. Samples from the Fiskenæsset area can easily be distinguished from samples from other investigated Greenlandic localities (Kalvig & Keulen, 2011).

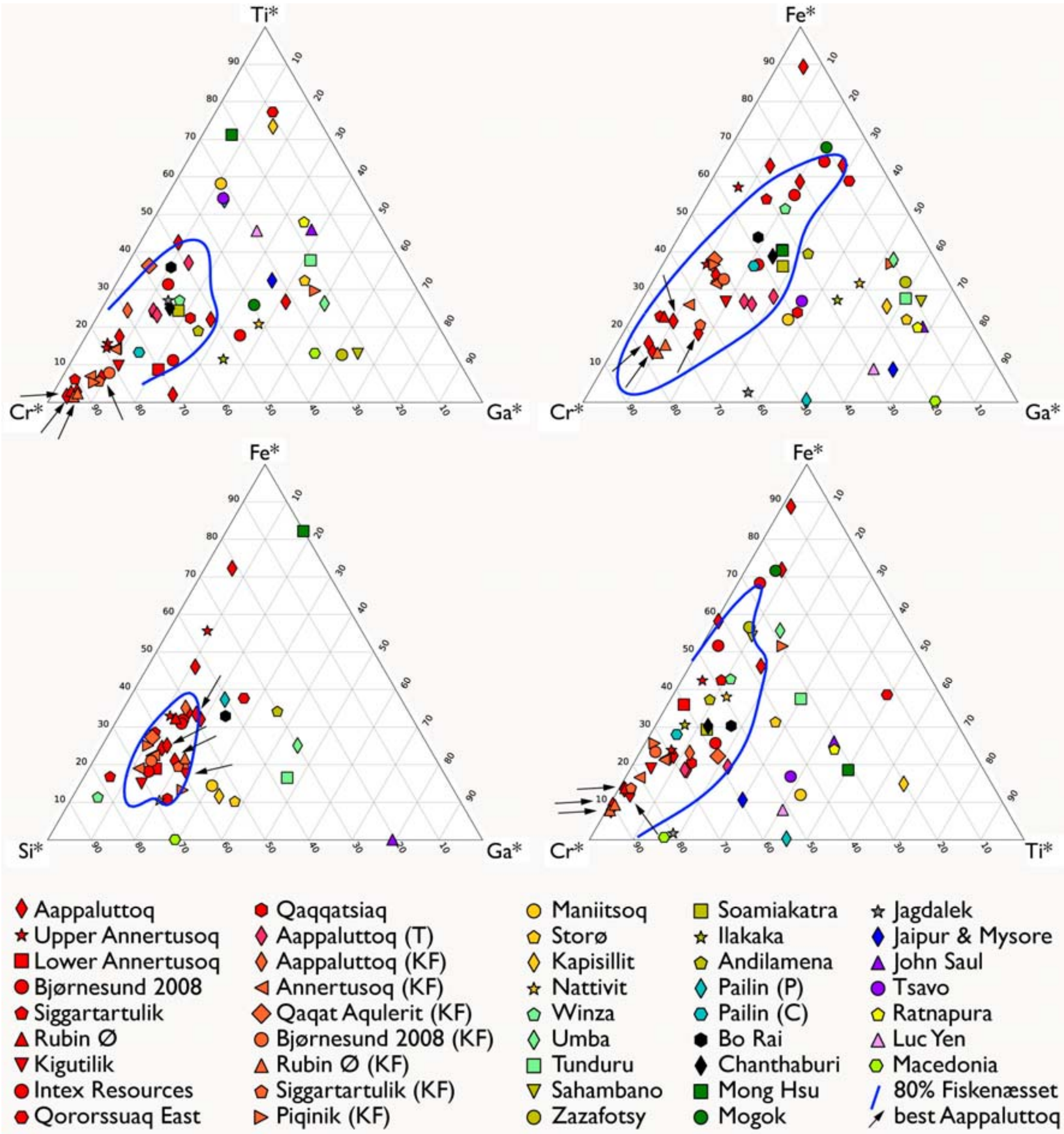


Fig. 3. Normalised trace element distributions for Ti-Cr-Ga (A), Fe- Cr-Ga (B), Fe-Si-Ga (C), and Fe-Cr-Ti (D) in ruby from Fiskenæsset. The data is compared to literature data on international and Greenlandic ruby occurrences (Calligaro, 1999; Calvo del Castillo, 2009; Kalvig & Frei, 2010; Pornwilard et al., 2011; Rakotondrazafy et al., 2008; Schwarz et al., 2008; Thirangoon, 2008). Initials of the authors' names were used where more than one study of the same locality exits. Different colours indicate different countries. Diagrams were created with WxTernary (Keulen & Heijboer, 2011). See text for further explanation of the blue circles and the black arrows.

To be able to use trace element investigations as a fingerprinting tool for rubies, it is necessary to investigate the amount of overlap between samples from Fiskenæsset and from other localities. The blue lines in Figure 3 include 80% (26 out of 32) of the samples from the Fiskenæsset area, based on sample distribution density contouring. Most samples from other localities plot outside the blue line, but an overlapping chemistry is found with samples from Soamiakatra, Ilakaka, and Andilamena in Madagascar, Bo Rai and Chanthaburi in Thailand, Pailin in Cambodia and Winza in Tanzania. Rubies from all these localities are hosted by ultramafic to mafic rocks or are found as placer deposits and might have been derived of such rocks.

However, if only the four most transparent and most intensively red-coloured samples from Aappaluttoq, Fiskenæsset, are taken into account, then no overlap with samples from other known ruby occurrences is observed. The samples from Aappaluttoq are regarded as near-gem ruby quality and will be the type of samples that will be sold from a potential mine. Trace element geochemistry with ICP-MS is therefore a helpful tool in the fingerprinting of Greenlandic rubies.

However, to ensure that the trace element properties for gemstone-quality ruby are similar to the current results of the best Aappaluttoq samples an investigation of gem-quality samples is needed. As can be seen in Figure 3, the data is skewed and trace-element concentration values, especially for Cr, are changing with the quality of the stones. The best quality Aappaluttoq samples (with arrows, in Figure 3) are the outliers in the total Fiskenæsset sample set (in blue), not the average of the studied samples.

Figures 4 and 5 show two trace element variation diagrams, which have been used in international studies on rubies and sapphire. Advantage of these plots over the ternary diagrams applied in Figure 3 is that absolute values for the measurements have been used. Figure 4 shows the data for individual measurements of samples from the Fiskenæsset complex. Figure 5 shows average values for the Fiskenæsset samples and international samples. In the latter Figure the four best samples of the Fiskenæsset complex, as discussed above, have been separated from the rest of the Fiskenæsset complex samples and are shown in red. In both diagrams, the Fiskenæsset samples very clearly plot in the metamorphic field.

Some samples plot in the field where possibly mantle derived sapphires from Yogo Gulch (USA) also plot (Figure 4A, 5A; Peucat et al. 2007). For comparison purposes however, one has to bear in mind that the Fe vs Ga/Mg plot originally was intended for blue sapphires. The samples from Fiskenæsset are as rich in Fe as blue sapphires are, but the position of the boxes were not calibrated for rubies. Compared to international samples, the samples from Aappaluttoq show an overlap with samples from mafic and ultramafic rocks in Mozambique and Tanzania (Figure 5A).

Figures 4b and 5b shows the variation for the oxides of the trace elements Cr, Ga, Fe, and Ti. Again the samples from Aappaluttoq plot close to samples from Winza, Umba, Nattivit and Mozambique. Results are consistant with the data of Kalvig & Frei (2010), but we do not find outliers in Mg, Fe, and Ga concentrations for the samples from the Fiskenæsset complex.

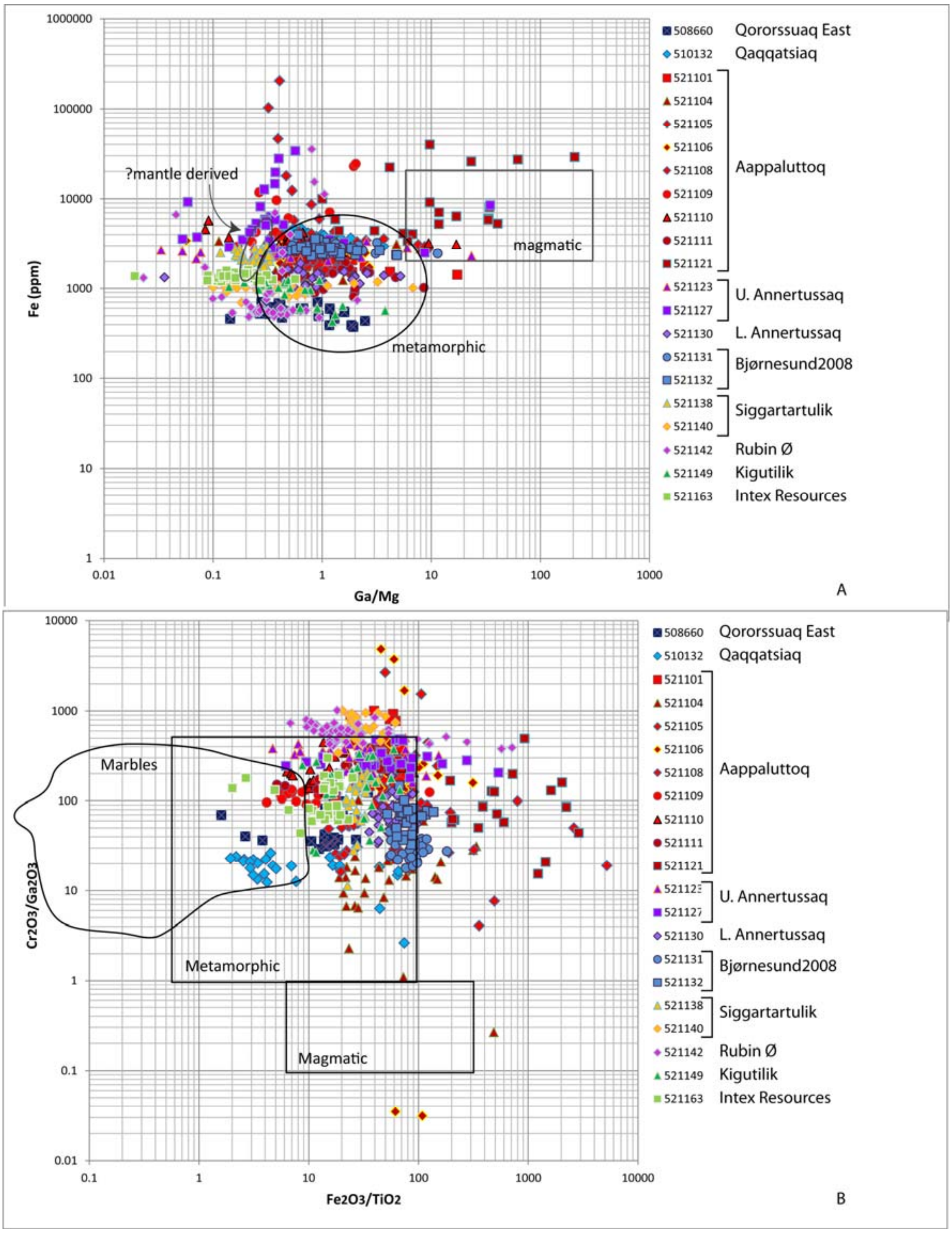


Figure 4: A. Fe vs Ga/Mg data for the ruby samples of the Fiskenæsset complex. The boxes are drawn after Peucat et al., 2007 and are originally intended for blue sapphires. B.Cr_2O_3/Ga_2O_3 vs Fe_2O_3/TiO_2 data for the ruby samples of the Fiskenæsset complex. The boxes are drawn after Sutherland et al. 2003 and Rakontondrazafy et al. 2008, based on data for rubies and sapphires.

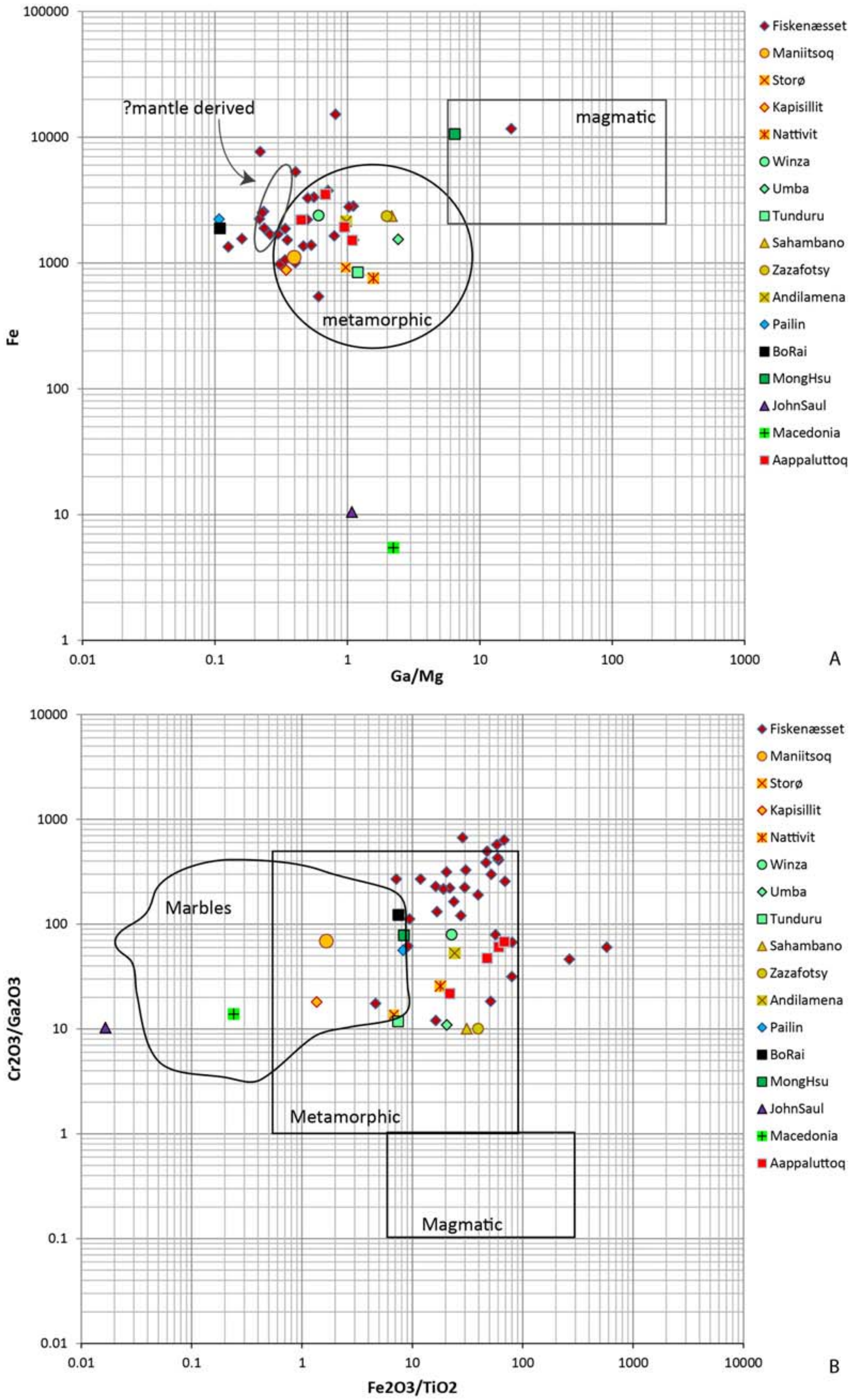


Figure 5: A. Average Fe vs Ga/Mg data for the ruby samples of the Fiskenæsset complex, compared with international occurrences. B.Average Cr_2O_3/Ga_2O_3 vs Fe_2O_3/TiO_2 data for the ruby samples of the Fiskenæsset complex, compared with international occurrences. See Figure 4 for references on the boxes. Literature data from the same sources as referred to in Figure 3.

4. Raman spectroscopy

A preliminary Raman Spectroscopy investigation was performed at the Department of Chemistry, Technical University of Denmark (DTU), in cooperation with Dr. Rolf W. Berg. The analyses were performed to characterise the Greenlandic rubies with a non-destructive method. Unfortunately, it seems that Raman spectroscopy does 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. The samples were very fluorescent, which disturbed the formation of clear peaks.

The analysis of a ruby sample from Morogoro, Tanzania, which is poorer in Cr, and a synthetic sapphire, shows that Raman spectroscopy works well for those (Figure 6).

Further investigations of the possibility to use Raman spectroscopy and other spectroscopy techniques on the Greenlandic rubies are planned.

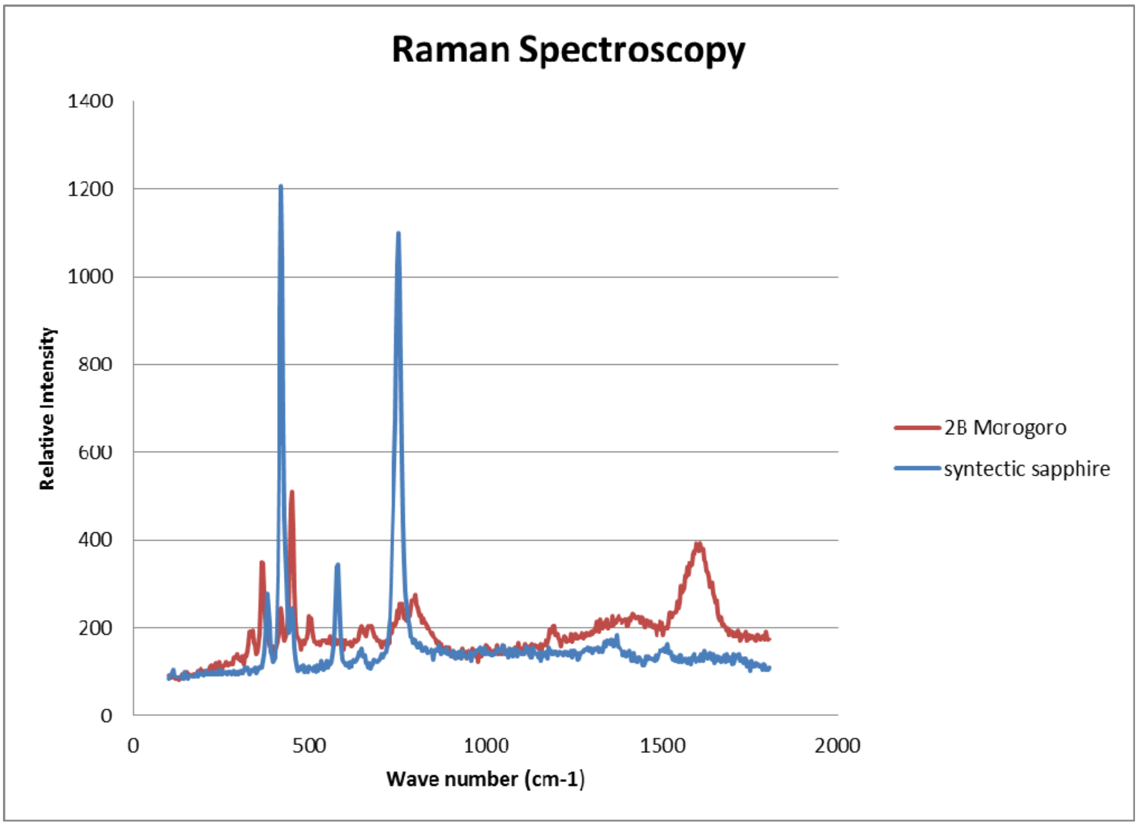


Figure 6: Raman spectroscopy results for a ruby from Morogoro, Tanzania, and for synthetic sapphire. Peaks depend on the crystallinity of the sample and the amount and type of trace elements in the sample.

5. Conclusions

Samples from Fiskenæsset are relatively high in Cr and Fe and low in 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 might 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, is necessary.

For a good fingerprinting more analytical parameters ought to be added:

- -Optical microscope observations and physical parameters (mineral characteristics)
- - Microprobe (chemistry & petrology)
- - FTIR or UVvis spectrometry (crystallography)
- - Scanning XRF (trace elements, non-destructive)

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.

6. Acknowledgements

This study is part of a collaboration project between the Bureau of Minerals and Petroleum in Nuuk, and GEUS. The authors wish to thank Tonny B. Thomsen for assistance on the Laser Ablation ICP-MS. Mojagan Alaei, Olga Nielsen and Michael Nielsen helped with the sample preparation. We are grateful for the help of Rolf Berg with the Raman spectroscopy.

Overview of the attachments

- Extended peer-revied abstract for the GIT conference in Thailand
- Powerpoint presentation of Keulen & Kalvig at the GIT conference in Thailand.
- Draft of an article submitted to the Review of the Surveys Activities. The final version is expected in late spring-early summer 2013.

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Oxygen isotopes and geochemical characteristics of corundum (ruby) from Fiskenæsset, Greenland – identification and origin determination

***Nynke Keulen*[1], *Per Kalvig*[1]**

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Extended Abstract

Since the late 1960s it has been know that pink corundum (ruby) exists in the area near Fiskenæsset (Qeqetarsuatsiaat), southern West-Greenland. The corundum is hosted in the Fiskenæsset Complex, which is part of the Archaean basement of the North Atlantic Craton. To date, circa 40 ruby localities are known in the area with a wide range of qualities – a few localities yield stones of gem quality. The most promising locality is likely to be mined in the nearest future by the Canadian company True North Gems. Red, pink and blue corundum (rubies and sapphires) are also known - in smaller quantities – from other areas in Greenland.

The Fiskenæsset complex units comprise a series of intrusive sheets of anorthosite, leucogabbro, gabbro, and ultramafic rocks (Windley *et al.*, 1973; Myers, 1985) that were interpreted as derived from a supra-subduction setting, while the associated amphibolites are of a mid-oceanic ridge to island arc basalt precursor composition (Polat *et al.*, 2009). The greater Fiskenæsset region was metamorphosed at mid- to upper amphibolite-facies temperatures and pressures, reaching granulite facies conditions near the village Fiskenæsset (McGregor & Friend, 1992; Schumacher *et al.*, 2011). At least one generation of felsic pegmatite sheets crosscut the anorthosite, ultramafic rocks, amphibolite, and gneisses and created reaction zones that develop aluminium-rich mineral assemblages derived from the aluminium in the anorthosite rocks. These reaction zone assemblages include very coarse-grained, radial anthophyllite ± green pargasite ± green or red spinel ± sapphirine ± cordierite (up to 30 cm single crystals) ± pink corundum, and ± phlogopite associated with pegmatitic felsic sheets and the ultramafic bodies (Schumacher *et al.*, 2011).

This study is a first attempt to find geochemical characteristics that can be used to tie the Greenlandic rubies to their area of origin. Here, we present laser ablation-ICP-MS trace element geochemistry data and oxygen isotope investigations on samples from the Fiskenæsset area and other known localities in Greenland (Storø, Maniitsoq, Kapisilit, Tasiilaq, and Nugtivit).

The trace element geochemistry investigations were concentrated on the elements Mg, Si, Ti, V, Cr, Fe, Ga, and Ge, as these elements are the most widely reported ones in international literature (Kalvig & Frei, 2010), but we made investigations on a wider range of elements. Plotting of the data for the first 25 samples in ternary diagrams for Fe, Cr, V, Ti, Ga, Mg, and Si, shows that the Fiskenæsset corundum (rubies) can be distinguished from other Greenlandic occurrences (Kalvig & Keulen, 2011). Samples from Fiskenæsset show a considerably higher amount of Cr than samples from other areas in Greenland, they are relatively rich in Fe, but relatively poor in Ti and Ga, while V, Mg and Si do not show very distinctive values compared to samples from other areas in Greenland.

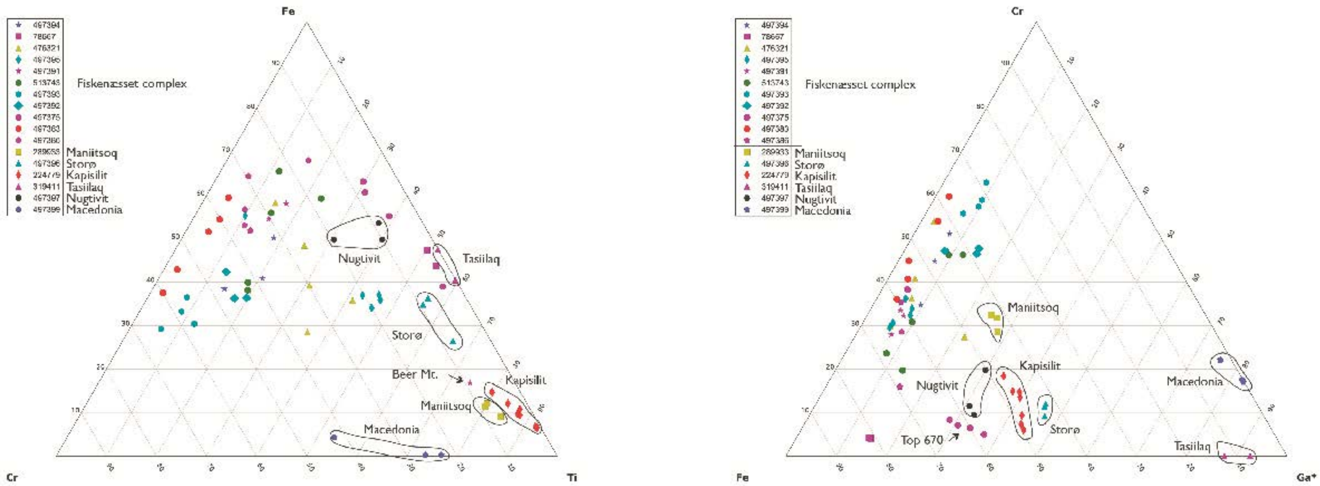

Figure 1: Normalised trace element distributions for Fe-Cr-Ti (left) and Cr-Fe-Ga (right) in corundum from Fiskenæsset and six other localities in Greenland. Diagrams were created with WxTernary (Keulen & Heijboer, 2011).

Oxygen isotope composition measurements were performed on 11 samples from Greenland at the University of Lausanne, Switzerland using an isotope ration mass spectrometer. Six of those samples stem from the Fiskenæsset region. δ^{18}O ratios vary between 1.62 and 4.20‰ for the Fiskenæsset area, which is low compared to the other areas in Greenland (up to 10.03‰ for Maniitsoq) with the exception of one sample from Nugtivit with 2.41‰. The δ^{18}O ratios are also low compared to most other investigated corundum deposits world-wide (Giuliani *et al.*, 2007). The lowermost ratios (δ^{18}O < 3‰) are nearly diagnostic for the Fiskenæsset area – world-wide only the placer deposits at Andilamena and Ilakaka, both in Madagascar and the cordieritite from Iankaroka, Madagascar have lower reported δ^{18}O ratios. Low ratios for δ^{18}O (4‰ and under) generally fit with rock types like mafic rocks, mafic gneiss, basalts, and desilicated pegmatite in mafic rocks (Giuliani *et al.*, 2005) and this is in excellent agreement with the mafic to ultramafic setting of the Fiskenæsset rubies.

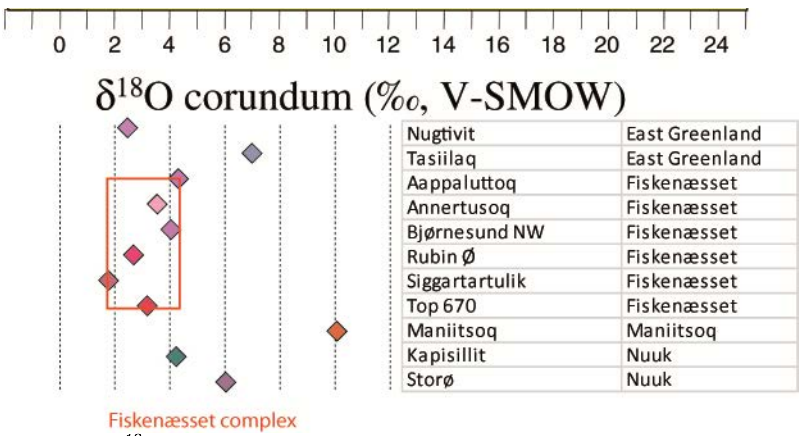

Figure 2: δ^{18}O ratios for six samples from Fiskenæsset (in the red box) and from five other localities in Greenland. The range of observed δ^{18}O ratios worldwide ranges from ca. 0 – 24‰.

Acknowledgements:
This study is part of a collaboration project between the Bureau of Minerals and Petroleum in Nuuk, Greenland and the Geological Survey of Denmark and Greenland, Copenhagen, Denmark. The authors wish to thank Kerstin Bauer and Torsten Vennemann for help with the oxygen isotope analyses, and Thomas F. Kokfelt and Tonny B. Thomsen for assistance on the Laser Ablation ICP-MS. Fiorella Fabra Aguilera, Mojagan Alaei, and Michael Nielsen helped with the sample preparation.

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G E U S

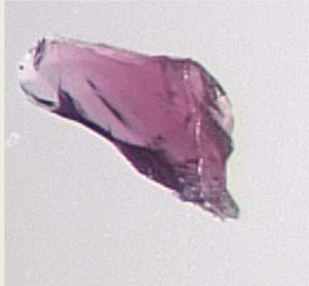
Oxygen isotopes and geochemical characteristics of corundum (ruby) from Fiskenæsset, Greenland

Identification and origin determination

Nynke Keulen & Per Kalvig

Geological Survey of Denmark and Greenland
Danish Ministry of Climate, Energy and Building

NAALAKKERSUISUT
GOVERNMENT OF GREENLAND



Background:

Pink sapphire (ruby) exists in the area near Fiskenæsset (Qeqetarsuatsiaat), southern West-Greenland.

Circa 40 ruby localities are known in the area with a wide range of qualities – a few localities yield stones of gem quality.

The most promising locality, Aappalutoq, is likely to be mined in the nearest future by the Canadian company True North Gems.

Collaboration project between the Bureau of Minerals and Petroleum in Nuuk, Greenland and the Geological Survey of Denmark and Greenland, Copenhagen, Denmark.

Why do geographical typing of corundum?

Factors affecting value:

- Carat
- Colour (hue, saturation, tone)
- Clarity
- Cut quality
- Supply
- Demand
- Geographic origin
- Type- and extent of treatment (high T and P heating/ lead-glass filing)
- Public confidence in the product (Certifications – Fair Trade etc.)

Gemstone issue:
•Conflict minerals - mined in conditions of armed conflict and human rights abuses
•Non-conflict minerals

Certification could:
•Add value to gemstones
•Create enhanced domestic processing of gemstones
•Support small-scale mining formalization efforts

Geographical typing

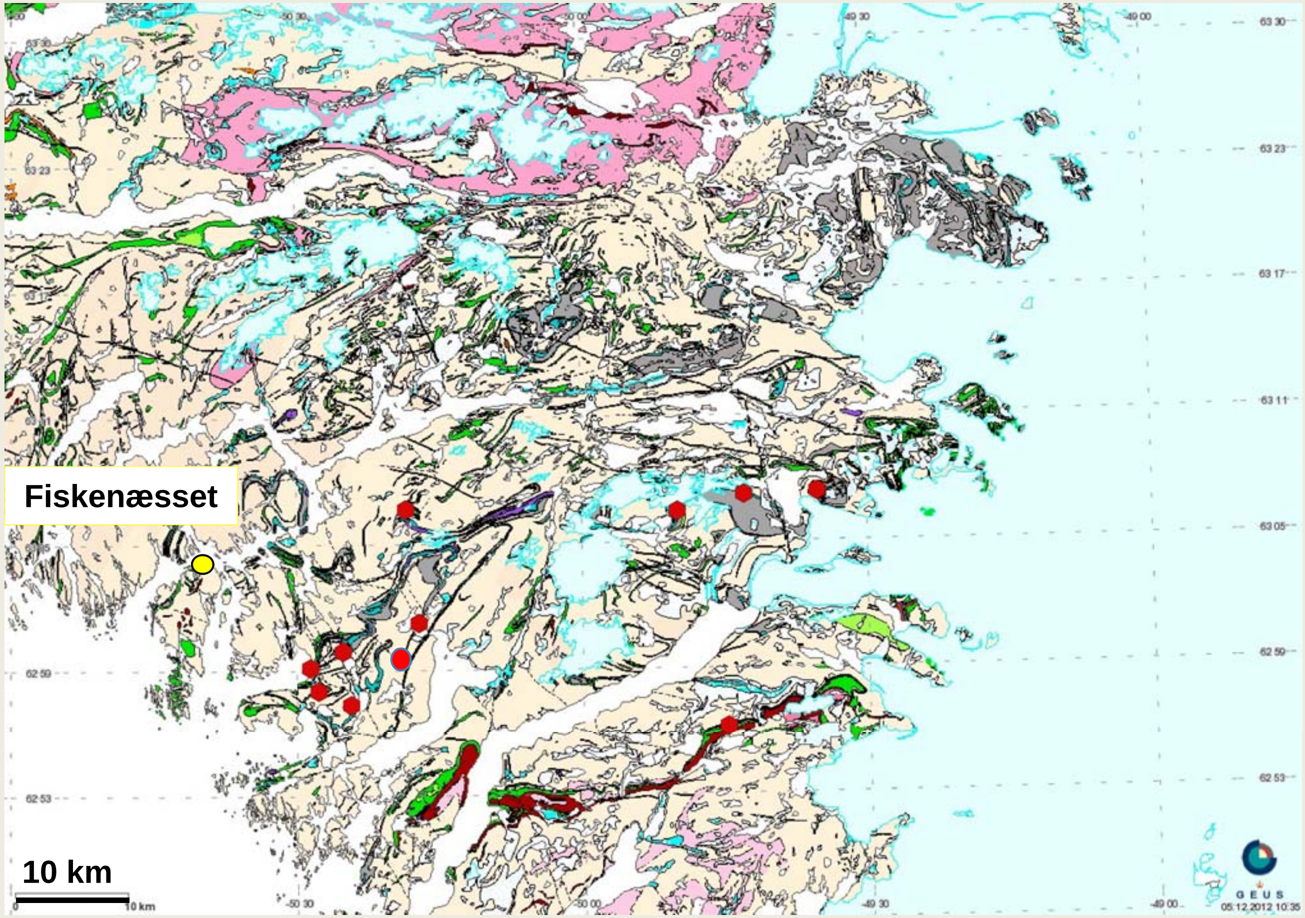
- Samples from GEUS collections
- No gem- or near-gem qualities investigated

- 32 samples (11 localities) from the Fiskenæsset complex
- 4 samples from other localities in Greenland:
    - Maniitsoq
    - Storø (Nuuk area)
    - Kapisillit (Nuuk area)
    - Nugtivit (East Greenland)

- Geochemical characteristics
- Oxygen isotopes

Fiskenæsset complex

- intrusive sheets of anorthosite, leucogabbro, gabbro, and ultramafic rocks
- derived from a supra-subduction setting
- metamorphosed at mid- to upper amphibolite-facies – granulite facies temperatures and pressures



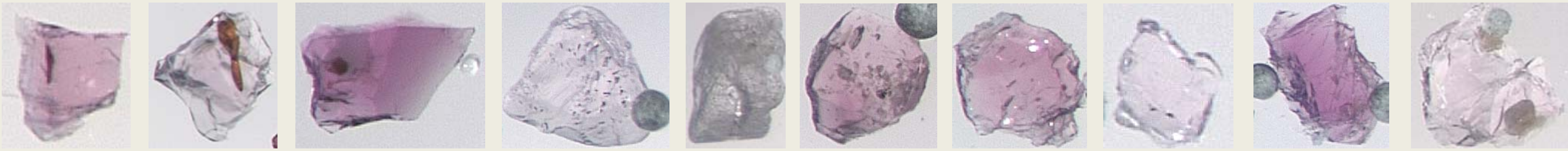
Geology: Windley *et al.,* 1973; Myers, 1985; Polat *et al.,* 2009; McGregor & Friend, 1992; Schumacher *et al.,* 2011.
Map: Keulen, Kokfelt et al. (2011)

Reaction:

Ultramafic rock + anorthosite + pegmatite -> corundum + amphibole ±biotite

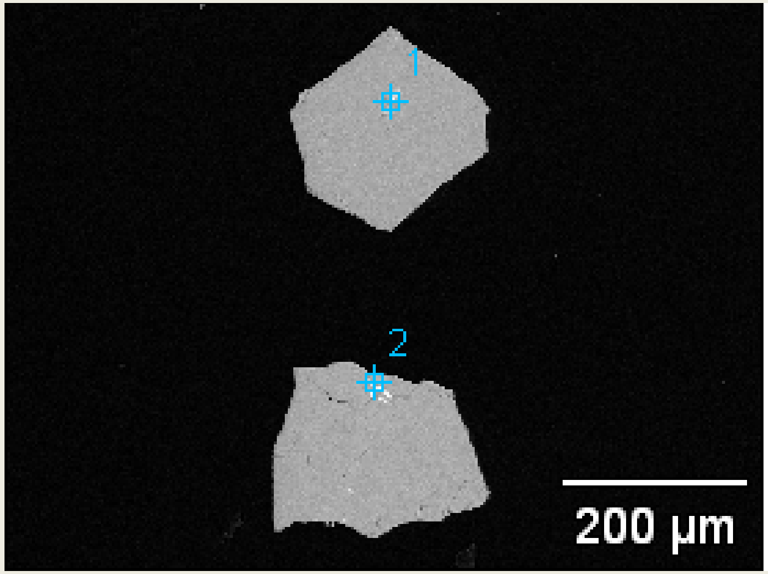
(1a) forsterite/serpentine + plagioclase => Ca-amphibole + "Al_2O_3" (component in Al-rich minerals) ± albite;
(1b) forsterite/serpentine + plagioclase + diopside => Ca-amphibole ± albite;
(2) forsterite/serpentine + SiO_2 (fluid) => anthophyllite;
(3) forsterite/serpentine + K-feldspar => biotite + anthophyllite;
(4) diopside + K-feldspar => biotite + calcic amphibole.
(5) "K-feldspar" (component in the fluid) + anthophyllite => biotite

Schumacher *et al.* (2011)



Common inclusions in Fiskenæsset corundum:

- •Spinel/Gahnite
- •Chromite
- •Rutile
- •Biotite
- •Gedrite, pargasite, anthophyllite
- •Sapphirine
- •Anorthite



•Determined with Energy dispersive X-ray spectroscopy on a Scanning Electon Microscope at Geological Survey of Denmark and Greenland

Trace elements (LA-ICP-MS data)

•Laser-ablation Inductively coupled plasma mass spectrometry analysis performed at the Geological Survey of Denmark and Greenland

•NIST612, NIST614, BCR2 standards

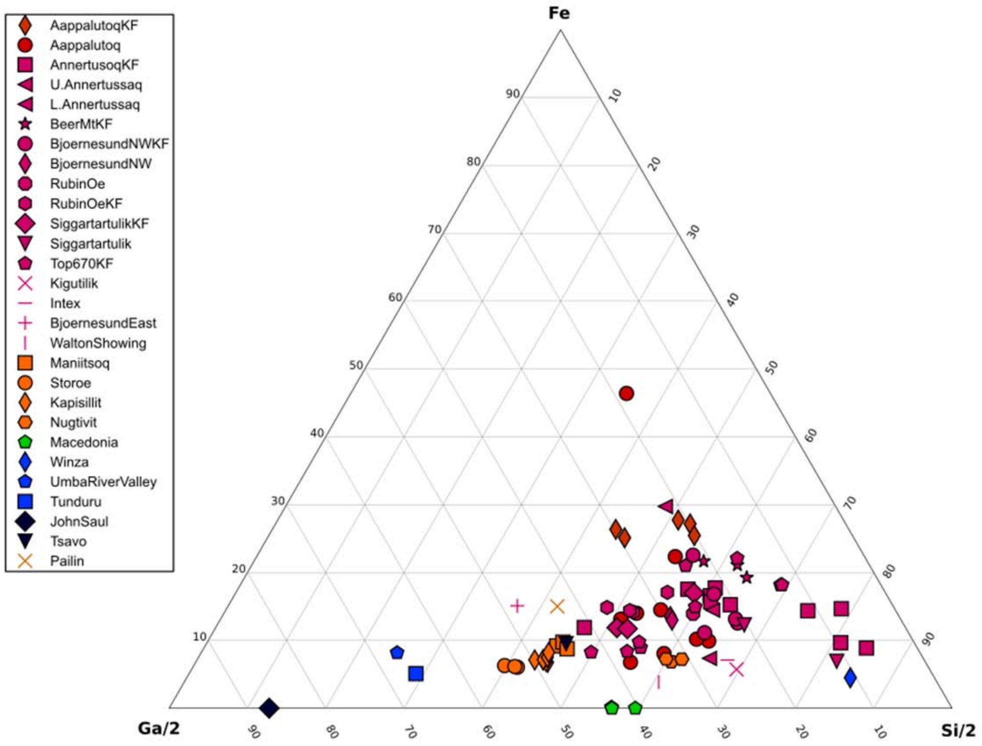
•Fe, Ti, Cr, V, Ga, Si, Mg

•Mn, Cu, Sn, Zr, Ge, Pb, Sr, Zn, Nb, Mo, Ba, La, Ce, Cs, Hf, Ta: no significant results

Trace elements (LA-ICP-MS data)

Based on Guilong & Günther (2001)
Data normalised with standard deviation

Fe



Ga

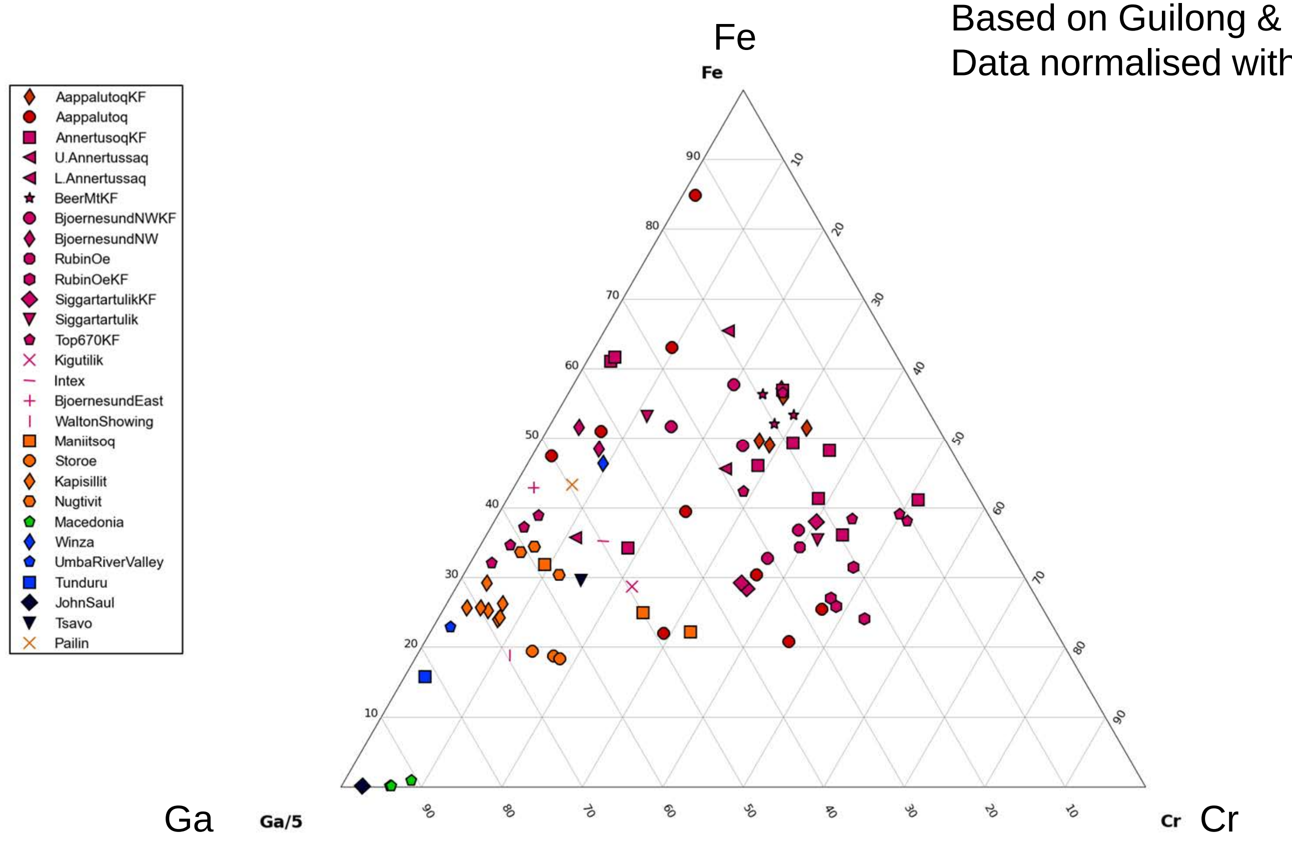
Si

Kalvig & Keulen (2011)
Kalvig & Frei (2010)
Pornwilard (2011)
Schwarz (2008)
Calligaro (1999)

The corundum from Fiskenæsset appears to be different from other Greenlandic corundum and many international corundum localities

Trace elements (LA-ICP-MS data)

Based on Guilong & Günther (2001)
Data normalised with standard deviation



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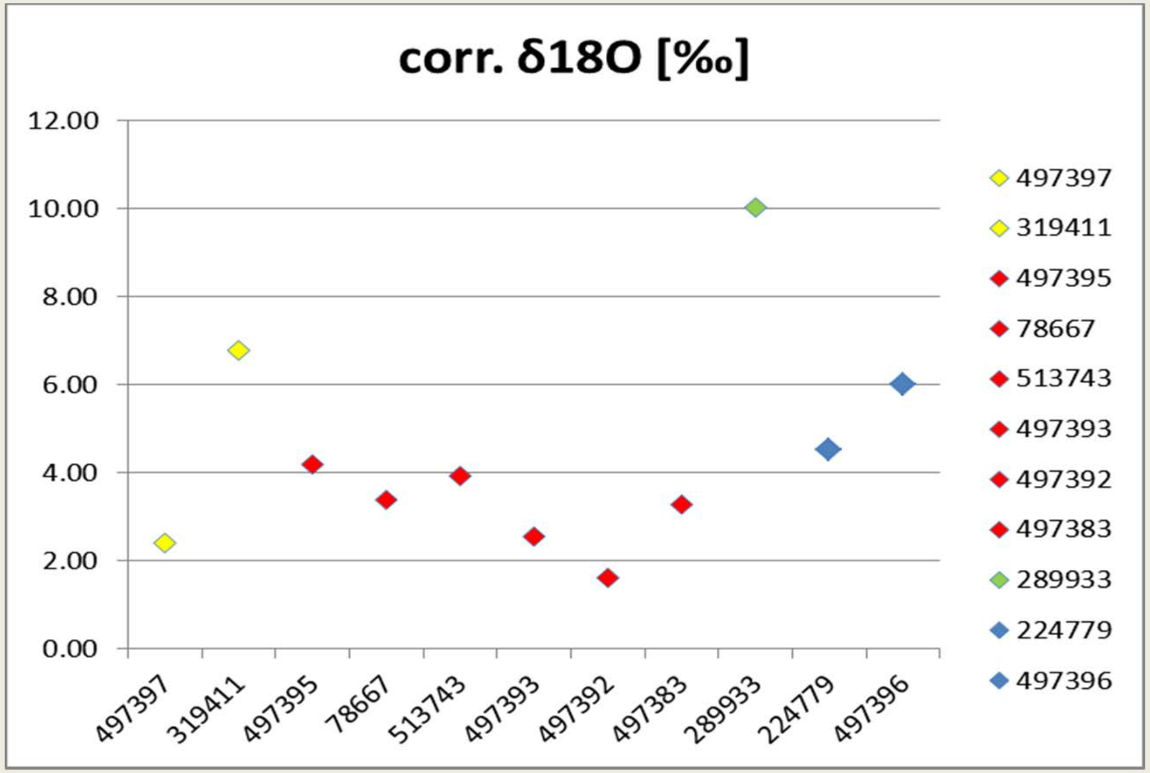
Oxygen isotope analysis
Corrected δ^{18}O-values in ‰ V-SMOW



East Greenland

Fiskenæsset

Maniitsoq

Nuuk / Godthåbsfjorden

Analyses performed at University of Lausanne, Switzerland

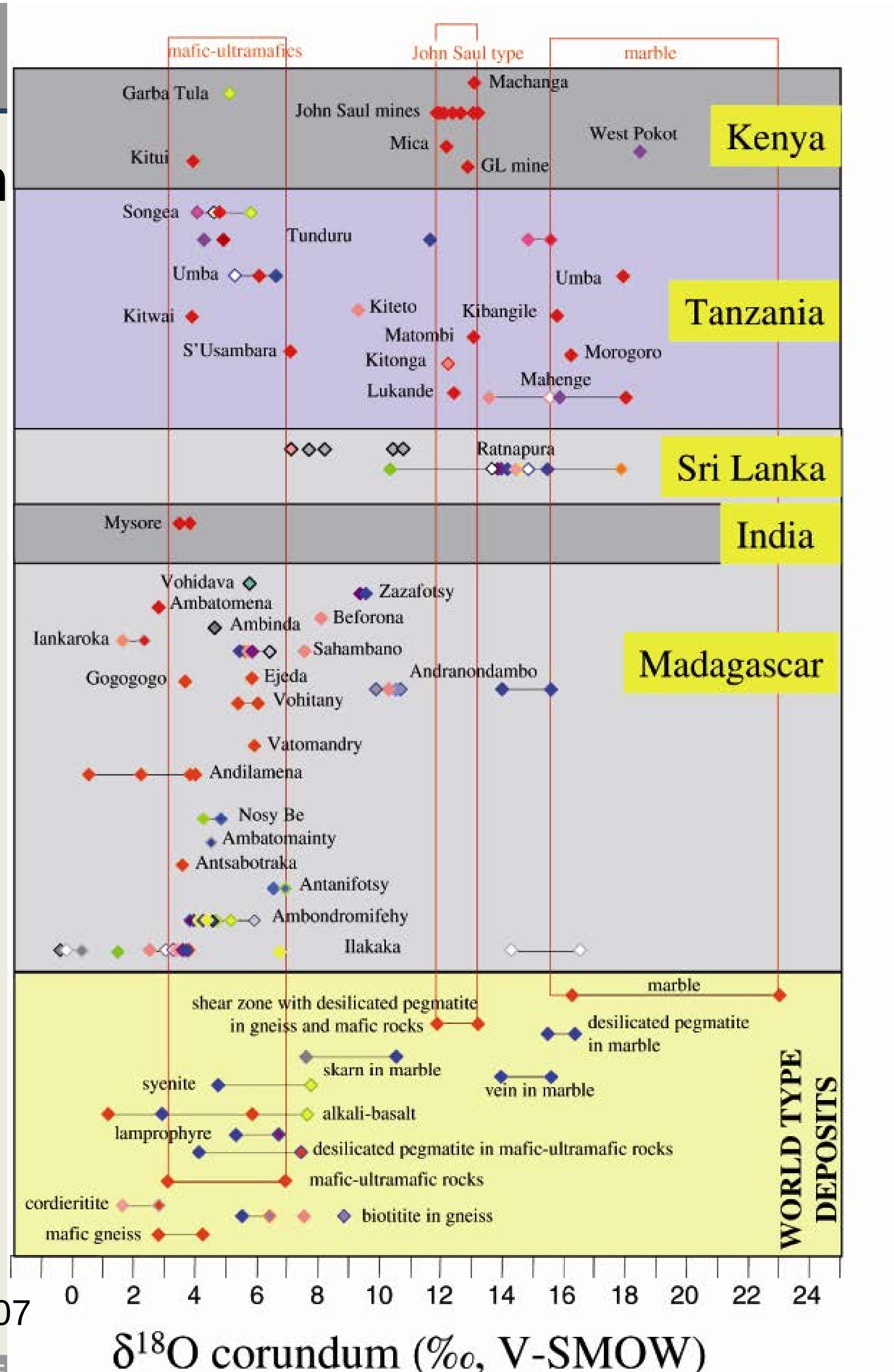
Kalvig & Keulen 2011

Oxygen isotope composition of corundum

Oxygen isotope composition of corundum from the different types of primary and secondary deposits of Madagascar, Kenya, Tanzania, Sri Lanka, and India.

The data reported in the conventional delta notation relative to V-SMOW are compared with the oxygen isotopic ranges defined for corundum types deposit worldwide.

Color in diamonds represents color for ruby (in red and pink) and colored sapphire (others). White diamonds represent colorless sapphires.



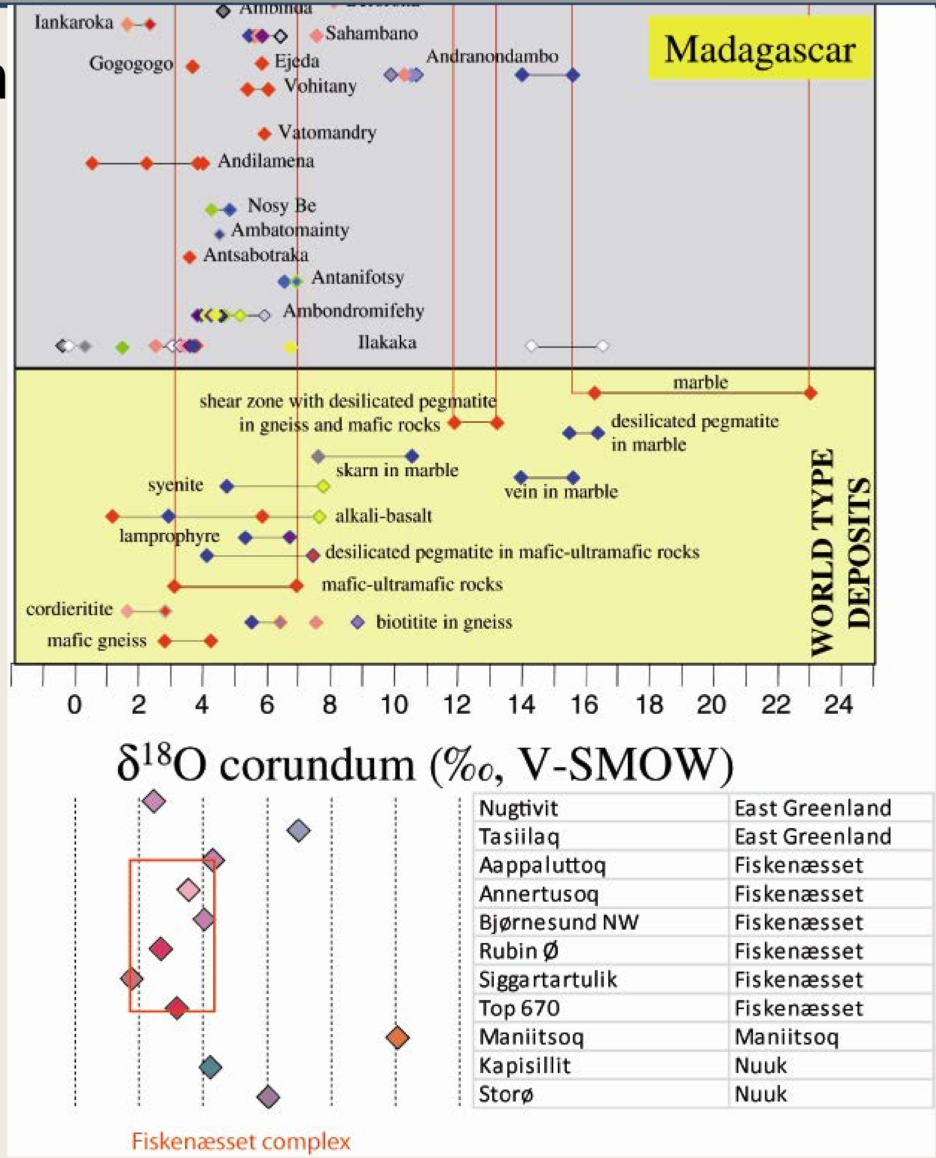
Giuliani et al. 2007

Oxygen isotope composition of corundum - Greenland

Fiskenæsset :
The $\delta^{18}O$ values (1.62 - 4.20‰) are low.

The $\delta^{18}O$ values largely overlap with the mafic-ultramafic values. This is in good agreement with the general thoughts that the gem-corundum is derived from a metamorphic reaction involving the anorthosite and ultramafic rocks (e.g. Herd et al. 1969, Herd 1973, Schumacher et al. 2011).

The lowermost values ($\delta^{18}O$ < 3‰) are nearly diagnostic for the Fiskenæsset complex – only a few deposits from Madagascar have lower reported $\delta^{18}O$ values.

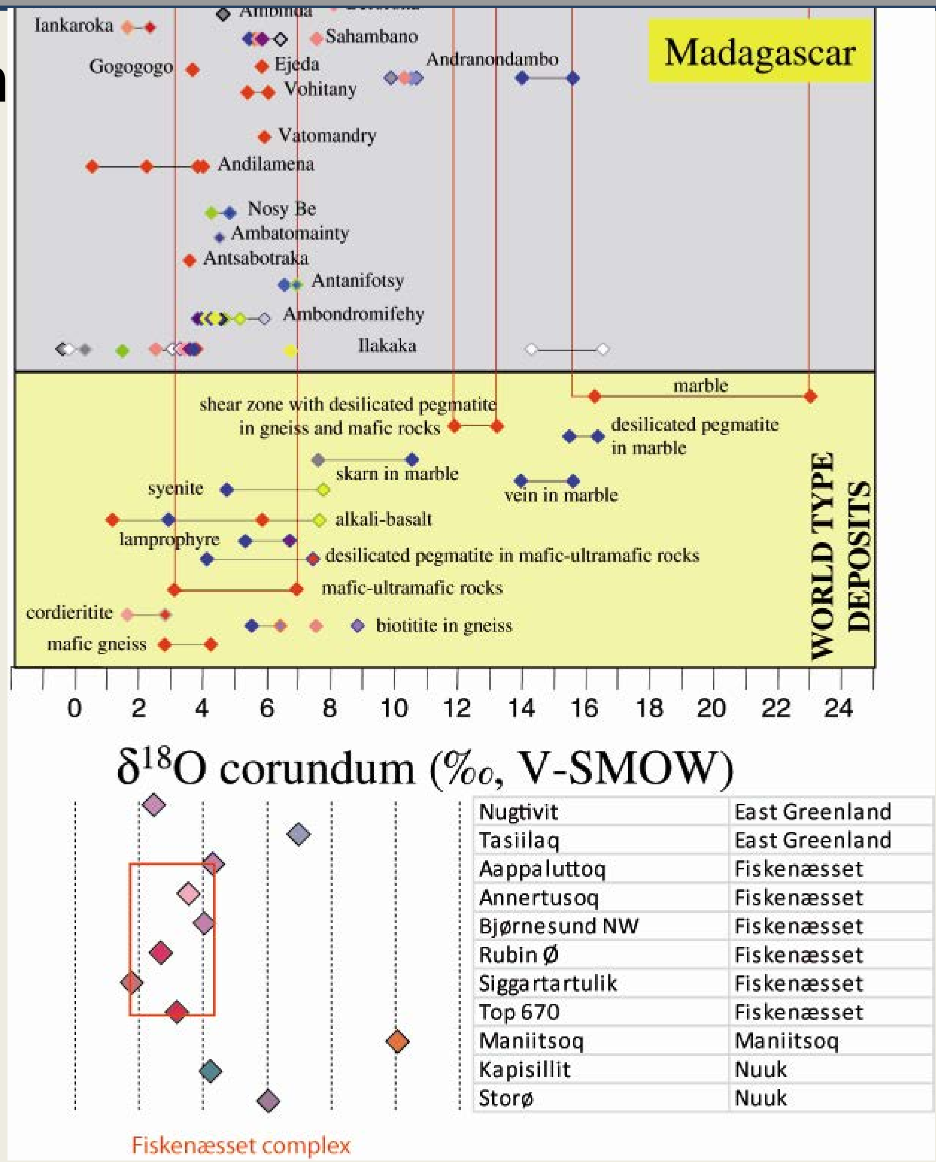


From: Kalvig & Keulen (2011)

Oxygen isotope composition of corundum - Greenland

The Nuuk area (Storø, Kapisillit):
The $\delta^{18}O$ values (4.5 – 6 ‰) lie within the mafic-ultramafic field.

No further geological information is known and data cannot be validated against field observations.



From: Kalvig & Keulen (2011)

Oxygen isotope composition of corundum - Greenland

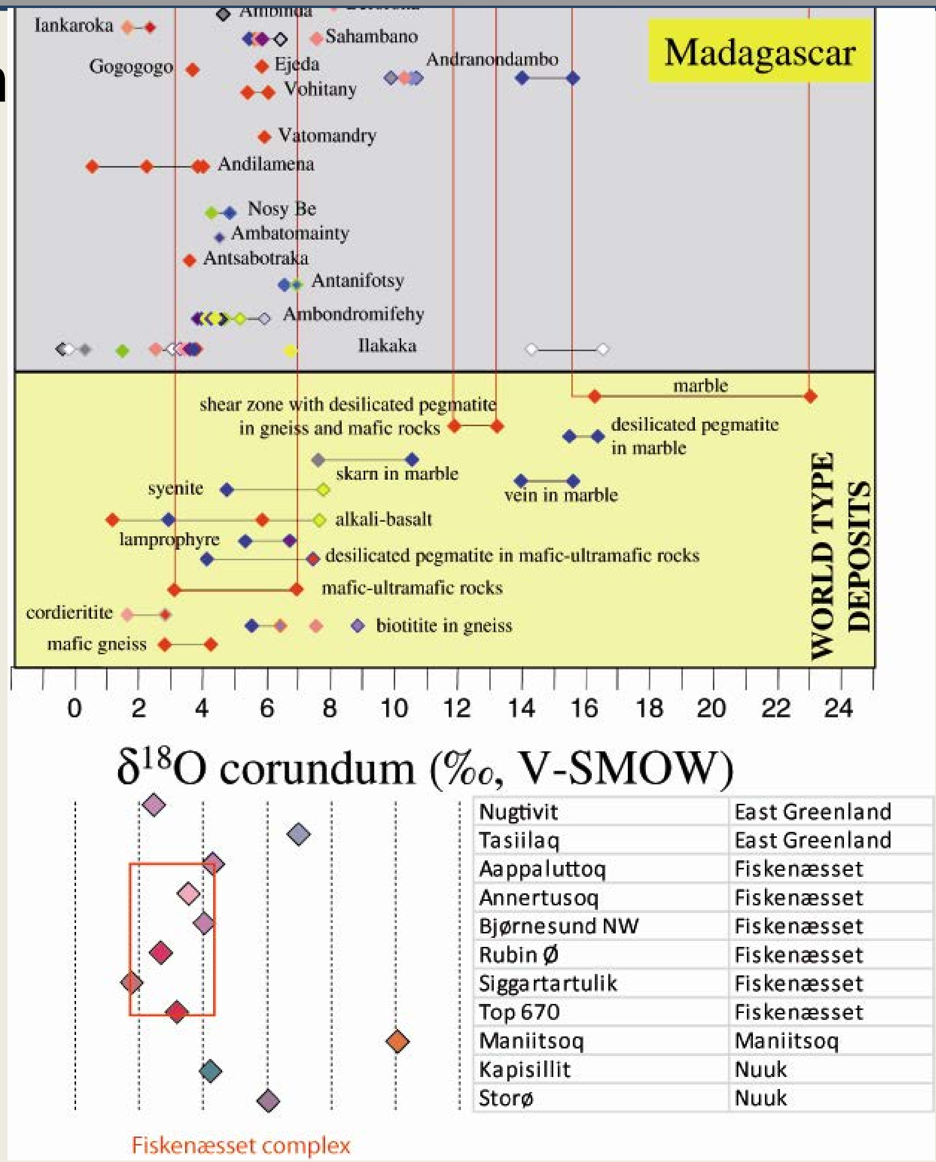
East Greenland - Nugtivit:
The $\delta^{18}O$ values (2.4‰) are low and overlap with the mafic-ultramafic values.

No further geological information is available for these samples and validation not possible.

Maniitsoq:
The value for $\delta^{18}O$ =10.03‰: typically related to skarns in marble, and to biotitite in gneiss related to a shear zone with high fluid activity.

Assumed to stem from sapphirine-bearing hornblendite.

The hornblendite was probably formed in a shear zone with high fluid activity (like the biotitites in Madagascar).



From: Kalvig & Keulen (2011)

Conclusions

- Corundum from the Fiskenæsset complex can be differentiated from other Greenlandic ruby occurrences based on the values for trace-elements Fe, Cr, Vi, Ti, Ga and Si.
- Samples from Fiskenæsset are relatively high in Cr and Fe and low in Ga and Ti

- Oxygen isotope ratios are a helpful parameter to characterise the gem-corundum. The $\delta^{18}O$ values for the Fiskenæsset complex lowers the previously reported range of $\delta^{18}O$ values for mafic-ultramafic rocks.
- $\delta^{18}O$ ratios vary between 1.62 and 4.20‰ for the Fiskenæsset area

- Typical inclusions are: spinel, chromite, biotite, amphiboles, rutile, sapphirine, anorthite. Verifications for gem-corundum is necessary

- For a good fingerprinting more analytical parameters ought to be added:
  - -Optical microscope observations (mineral characteristics)
  - - Microprobe (chemistry)
  - - Raman spectrometry (crystallography)
  - - Scanning XRF
- It is necessary to build up a database with all available analytical information on rubies from Greenland and elsewhere.

Fingerprinting of corundum (ruby) from Fiskenæsset, Greenland

Nynke Keulen, Per Kalvig

Since the late 1960s it has been know that pink corundum (ruby) exists in the area near Fiskenæsset (Qeqetarsuatsiaat) in southern West-Greenland. The corundum is hosted in the Fiskenæsset complex, which is part of the Archaean basement of the North Atlantic Craton. To date, c. 40 corundum localities are known in the area with a wide range of qualities – a few localities yield stones of gem quality. The most promising locality, Aappaluttoq, is likely to be mined in the nearest future by the Canadian company True North Gems (Figs 1, 2A). Red corundum of gem quality is called ruby; gem quality corundum of other colours (e.g. pink, yellow or blue) is called pink sapphire, yellow sapphire etc., while the blue gem corundum is saphhire. Red, pink and blue corundum are also known in smaller quantities from other areas in Greenland.

The Fiskenæsset complex

The Fiskenæsset complex units (Fig. 1) comprise a series of intrusive sheets of anorthosite, leucogabbro, gabbro and ultramafic rock (Fig. 1; Myers 1985). The Fiskenæsset complex units are interpreted as derived from a supra-subduction setting, while the associated amphibolites are of a mid-oceanic ridge to island arc basalt precursor composition (Polat et al. 2009). The greater Fiskenæsset region was metamorphosed at mid- to upper amphibolite-facies temperatures and pressures, reaching granulite facies conditions near the village Fiskenæsset (McGregor & Friend 1992; Schumacher et al. 2011). At least one generation of felsic pegmatite sheets crosscuts the anorthosite, ultramafic rocks, amphibolite, and gneisses and created reaction zones that developed aluminium-rich mineral assemblages derived from the aluminium in the anorthosite rocks (Fig. 2B). These reaction zone assemblages include very coarse-grained, radial anthophyllite ± green pargasite ± green or red spinel ± sapphirine ± cordierite (up to 30 cm single crystals) ± pink corundum, and ± phlogopite associated with pegmatitic felsic sheets and the ultramafic bodies (Schumacher et al. 2011).

This study is a first attempt to find geochemical and mineralogical characteristics that can be used to tie the Greenlandic rubies to their area of origin. This may have practical implications in the event a Greenlandic operation of rubies and pink-saphhire is established. Here, we present laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) trace element geochemistry data and oxygen isotope investigations of samples from the Fiskenæsset area and other known localities in Greenland (Storø, Maniitsoq, Kapisillit and Nugtivik).

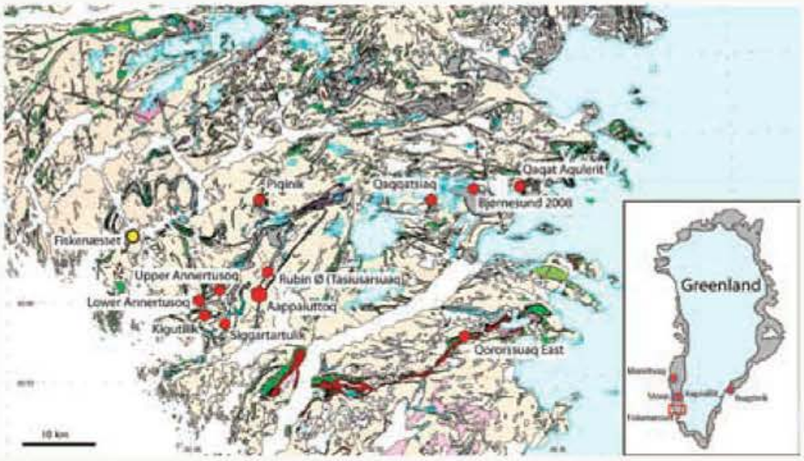


Fig. 1. Simplified geological map of the central part of the North Atlantic craton in southern West Greenland near the village Fisknæsset showing the investigated pink corundum (ruby) localities in the Fiskenæsset Complex. Map after Keulen & Kokfelt et al. (2011), see weblink for legend.

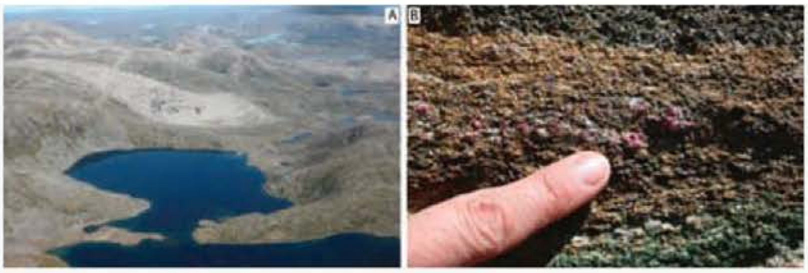


Fig. 2.A: Aappaluttoq, Fiskenæsset as seen from the helicoptor towards the north. The white-greyish rock is anorthosite B: Rubies in their host rock at Tasiussarsuaq, Fiskenæsset, Greenland.

Trace element geochemistry

Corundum has the chemical formula Al2O3 and like most other minerals usually includes very small quantities of other elements in its crystal structure. The amount of these trace elements and their ratios depend on the geological conditions during the formation of the corundum and vary therefore between individual corundum deposits. The concentrations of 24 different elements were measured with laser ablation-ICP-MS, however most of the analysed elements were not detected in the samples. Trace element geochemistry investigations of the Greenlandic corundum were concentrated on the elements Mg, Si, Ti, V, Cr, Fe, and Ga, as these elements are present in significant amounts and also the most widely reported ones in literature. We used the laser ablation sector-field inductively coupled plasma mass spectrometer (LA-SF-ICP-MS) at the Geological Survey of Denmark and Greenland (Frei & Gerdes 2009; Kalvig & Frei 2011), employing an ELEMENT 2. Data reduction and determination of concentrations were calculated off-line through the software Iolite using the Trace_Elements_IS routine (Hellstrom et al. 2008). Further details on the methods are found in Keulen & Kalvig (2013).

Results on the trace element investigations of 21 samples from ten localities in the Fiskenæsset complex are shown with red symbols in the ternary diagrams in Fig. 3. The data for corundum from the Fiskenæsset complex are in good concordance with earlier data from the area (Kalvig & Frei

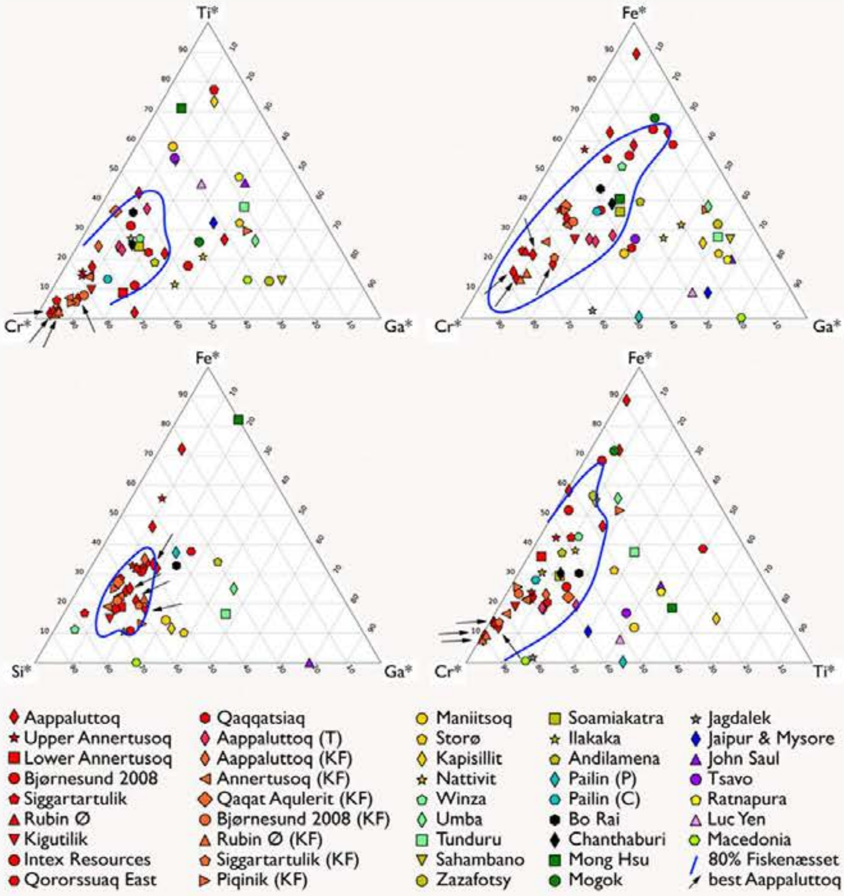
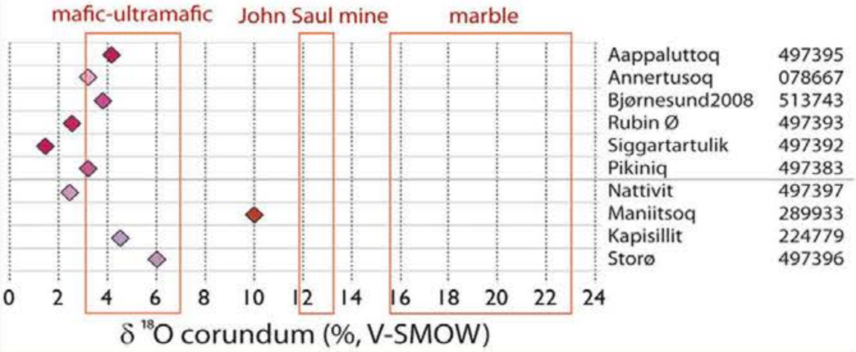


Fig. 3. Normalised trace element distributions for Ti-Cr-Ga (A), Cr-Fe-Ga (B), Fe-Si-Ga (C), and Fe-Cr-Ti (D) in corundum from Fiskenæsset. The data is compared to literature data on international and Greenlandic corundum occurences (Calligaro, 1999; del Castillo, 2009; Kalvig & Frei, 2010; Pornwilard, 2011; Rakontondrazafy, 2008; Schwarz, 2008; Thirangoon, 2008). Initials of the authors' names were used where more than one study of the same locality exits. Different colours indicate different countries. Diagrams were created with WxTernary (Keulen & Heijboer, 2011).

Fig. 4. ⊠18O ratios for six samples from Fiskenæsset and from four other localities in Greenland. Data values are expressed relative to VSMOW (Vienna Standard mean ocean water – the internationally used value for ⊠18O=0) in permil (‰). Colours indicate the approximate colour of the stones. Red boxes and classification as mafic-ultramafic, John Saul mine, and marble after Giuliani et al. (2007).



2010; Thirangoon 2008). In Fig. 3 data are compared with data from other samples from Greenland and samples from internationally, well-known, ruby occurences. Samples from Fiskenæsset show a considerably higher amount of Cr than samples from other areas in Greenland and most international samples. The Fiskenæsset rubies are relatively rich in Fe and Si, but relatively poor in Ti and Ga, while V and Mg do not show very distinctive values compared to samples from other areas. The trace element pattern in the samples from the Fiskenæsset area is different from other Greenlandic localities, and can easily be distinguished (Kalvig & Keulen 2011).

To be able to use trace element investigations as a finger printing tool for rubies it is necessary to investigate the amount of overlap between samples from Fiskenæsset and other localities. The blue lines in Fig. 2 include 80% (26 out of 32) of the samples from the Fiskenæsset area, based on sample distribution density contouring. Most samples from other localities plot outside the blue line, but an overlapping chemistry is found with samples from Soamiakatra, Ilakaka, and Andilamena in Madagascar, Bo Rai and Chanthaburi in Thailand, Pailin in Cambodia and Winza in Tanzania. Rubies from all these localities are hosted by ultramafic to mafic rocks or are found as placer deposits. This indicates that the trace elements from the rubies derive from the ultramafic rocks associated with the anorthosite.

However, if only the four most transparent and most intensively red-coloured samples from Aappaluttoq, Fiskenæsset, are taken into account, then no overlap between these samples and samples from other known ruby occurences is seen. These samples are closest in transparency and colour to the stones that will be sold from a potential mine and therefore represent the Aappaluttoq signature. As these samples have a distinct composition, trace element geochemistry with ICP-MS is a helpful tool in the fingerprinting the Greenlandic rubies.

Oxygen isotope geochemistry

Oxygen isotope composition measurements were performed on ten samples from Greenland at the University of Lausanne, Switzerland using an isotope ratio mass spectrometer. The oxygen isotope composition of the samples were measured using a method similar to that described by Kasemann et al. (2001), see Keulen & Kalvig (2013) for details.

Six of the samples come from the Fiskenæsset complex. The δ18O values vary between 1.62 and 4.20‰ for the Fiskenæsset area, which is low compared to the other areas in Greenland (up to 10.03‰ for Maniitsoq) with the exception of one sample from Nugtivit (2.41‰; Fig. 4). The δ18O values are also low compared to most other investigated corundum deposits world-wide (Giuliani et al. 2007). The lowermost values (δ18O <3‰) are nearly diagnostic for the Fiskenæsset area – world-wide only the placer deposits at Andilamena and Ilakaka, both in Madagascar and gem-corundum in a cordieritite from Iankaroka, Madagascar have lower reported δ18O values. Low δ18O values (≤4‰) generally reflect rock types such as mafic rocks, mafic gneiss, basalts, and desilicated pegmatite in mafic rocks (Giuliani et al. 2005) and this is in excellent agreement with the mafic to ultramafic setting of the Fiskenæsset rubies. The values for samples from Nugtivik, Kapisillit and Storø are also low (2.4, 4.5 and 6.0‰ respectively) and also plot in the mafic-ultrafic field. Unfortunately, no further geological information is available for these specimens and the data can thus not be validated against field observations. The value for Maniitsoq with δ18O =10.03‰ is typically related to skarns in marble, or to biotitite in gneiss related to a shear zone with high fluid activity. The rubies in the investigated sample are assumed to stem from sapphirine-bearing hornblendite. The hornblendite was probably formed in a shear zone with high fluid activity (like the biotitites in Madagascar).

The low δ18O values can also be used for fingerprinting Greenlandic rubies, especially the very low values for the Fiskenæsset complex and Nugtivik, as only few other international occurences have such low values.

Conclusions

High confidence fingerprinting of rubies requires a combination of independent analytical methods such as trace element analyses, oxygen isotope analyses and other studies. The two discussed methods are efficient to characterise the Fiskenæsset rubies. The ongoing research is focussing on optical and physical characteristics, spectroscopy methods and scanning XRF.

Acknowledgements

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