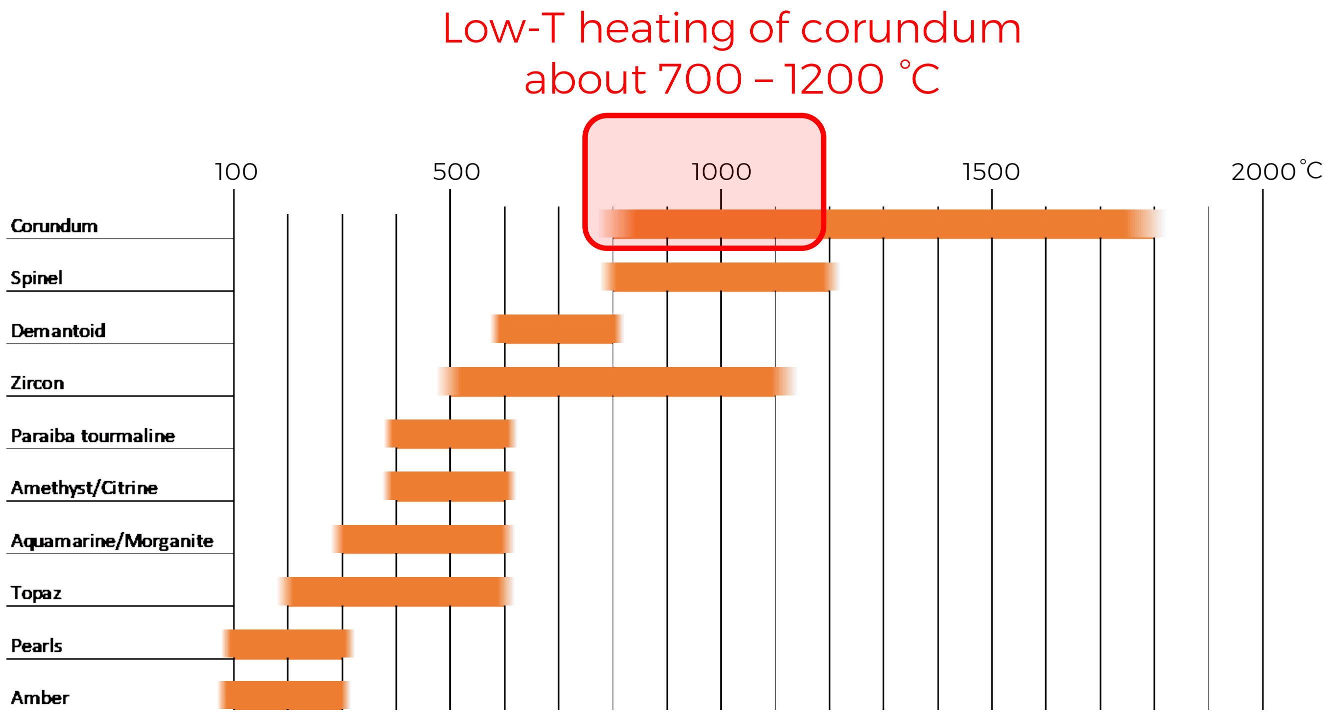
# Detection of Low-Temperature Heat Treatment in Corundum: Possibilities and Challenges

Dr. Michael S. Krzemnicki

Director, Swiss Gemmological Institute SSEF

# Heat Treatment of Corundum



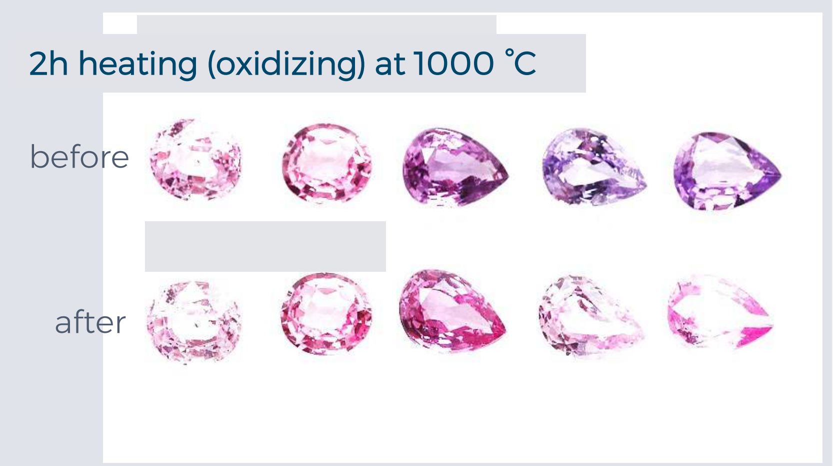

*approx. temperature ranges as by gemmological literature*

- In most cases, heat treatment results in a change/shift of colour.
- The lower the heating temperature the more challenging is its detection!

# Heat Treatment of Corundum

Unheated ruby from Mozambique.

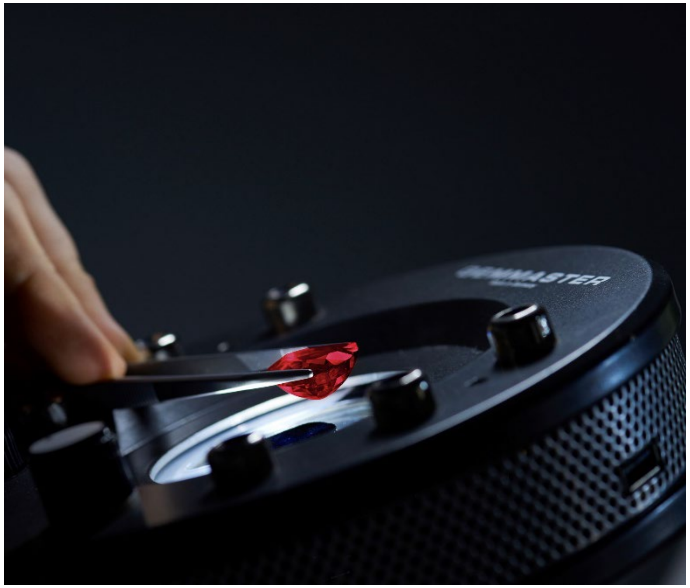
Heat treatment at low temperatures mostly applied to remove bluish zones and slightly shift purplish sapphires to a pink colour.

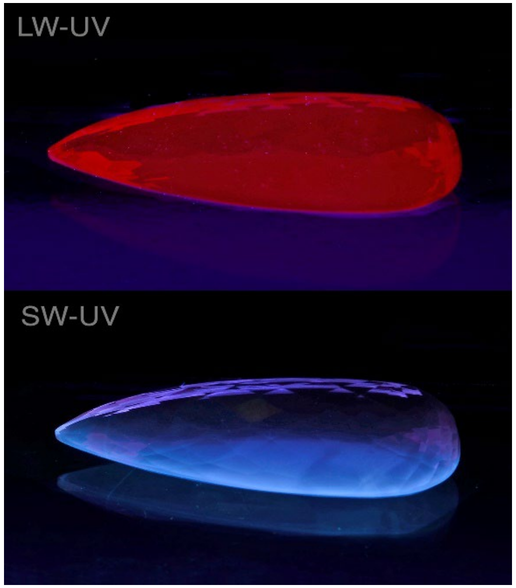


# Detection of Heat Treatment

No magic “black box” for
heat treatment detection !

# Detection of Heat Treatment




Always a combination of ‘classic’ microscopy, UV reaction, and spectroscopic analyses (Infrared- and Raman spectroscopy).

# Detection of Heat Treatment: 'Classic' Methods

## Microscopy

'Classic' heat treatment — Low-temperature heat treatment

Atoll-structures (discoid extension features) and "spotted" platelets are among those microscopic features indicating a heat treatment process.

**However, such characteristic features are often absent or very difficult to see, specifically in stones heated at lower temperatures (< 1000 °C)**

# Detection of Heat Treatment: 'Classic' Methods

## UV Reaction

Heated sapphire (Sri Lanka)

Heated ruby (Mong Hsu, Myanmar)

"chalky" whitish reaction under shortwave ultraviolet may indicate a heat treatment (at higher temperatures).

**However, most heated corundum will not show such reaction (and even certain unheated stones may show similar whitish UV reactions!**

# Detection of Heat Treatment: 'Classic' Methods

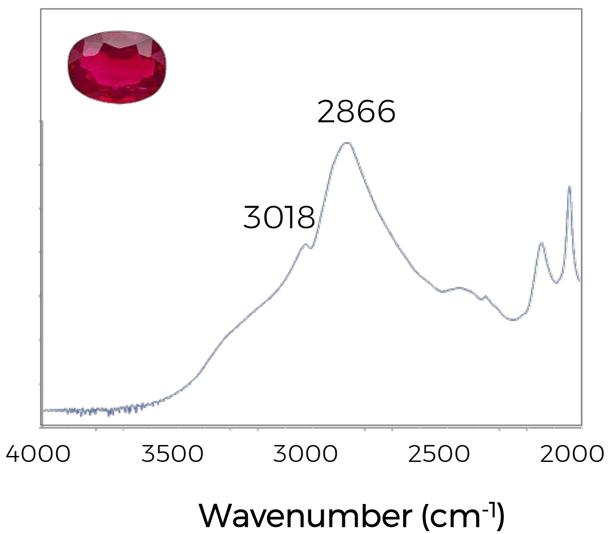
## Summarising: Classic detection methods Microscopy and UV reaction

- Microscopy remains to date very important for heat treatment detection.
- Obvious alterations of inclusions usually can be observed after heating at higher temperatures (beyond 1200 °C).
- In case of low-temperature heated stones, evident features for such treatment are often rather difficult to see or even absent.
- The same applies for stones which have no inclusions at all.

# Detection of Heat Treatment: Infrared Spectroscopy

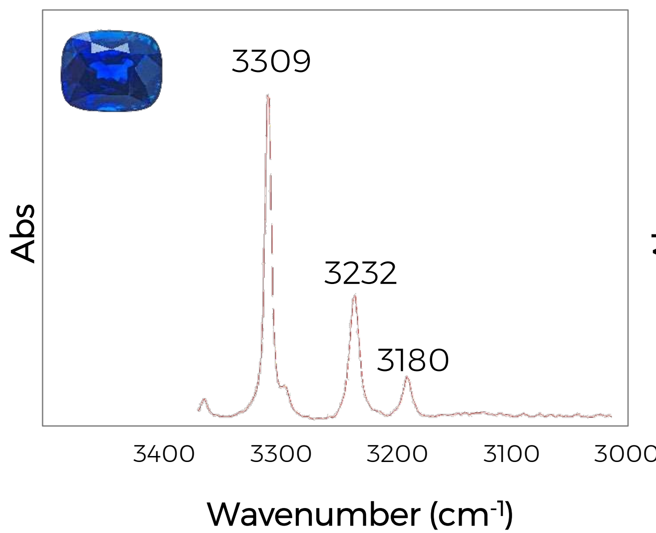
## Infrared Spectroscopy (FTIR)

Unheated Ruby



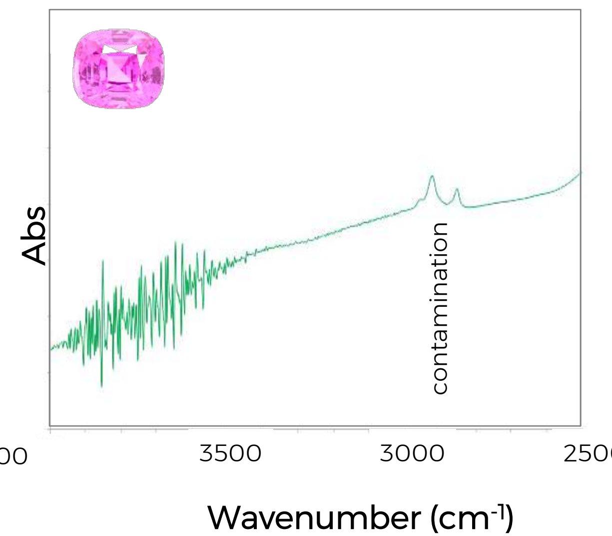

Diaspore related bands

Heated Sapphire




Ti$^{4+}$- OH$^{-}$ related peaks

??

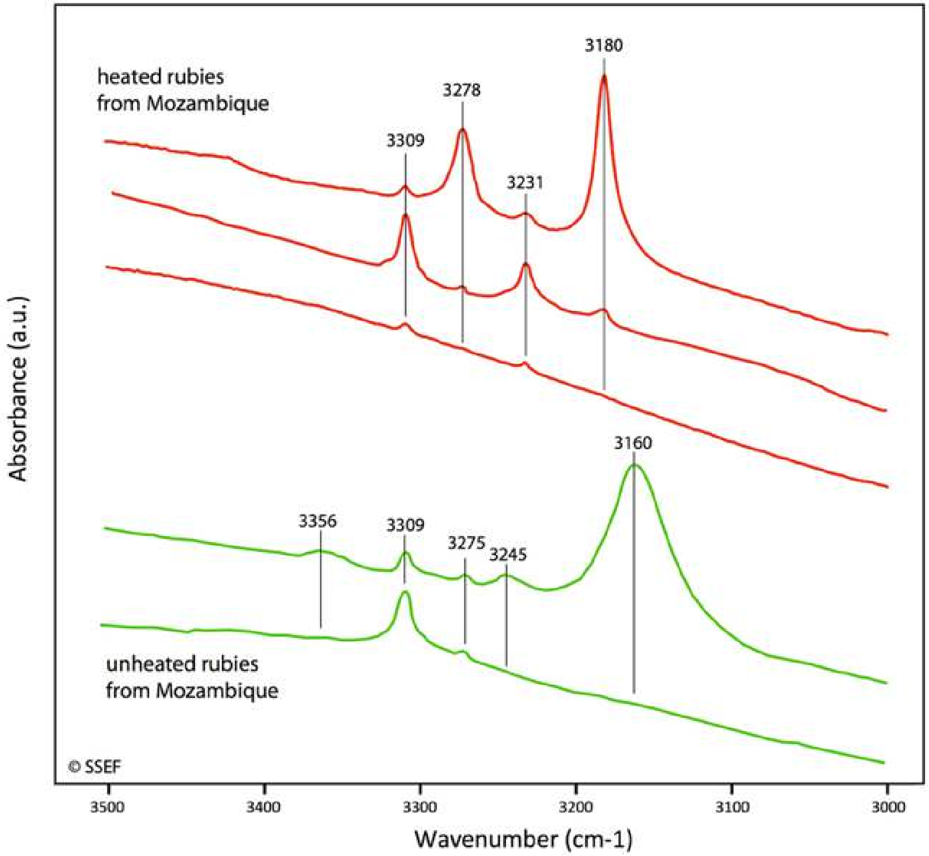



No signal indicating heat or no heat

# Detection of Heat Treatment: Infrared Spectroscopy

## Infrared Spectroscopy (FTIR) of unheated and heated Corundum

**FTIR-Spectra of Mozambique Rubies**

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SWISS GEMMOLOGICAL INSTITUTE
INSTITUT SUISSE DE GEMMOLOGIE

PRESS RELEASE

FOR IMMEDIATE RELEASE
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**New research by SSEF studies methods for detecting low-temperature heated rubies from Mozambique**

BASEL, SWITZERLAND: SEPTEMBER 12, 2018 – Since their discovery in early 2009, the ruby deposits near Montepuez in Mozambique have produced an impressive number of exceptional-quality stones, including iconic unheated gems such as the Rhino Ruby (22.04 cts), the Scarlet Drop (15.95 cts) and the Eyes of the Dragon (a pair of rubies weighing 11.26 cts and 10.70 cts), all of which were analysed by the Swiss Gemmological Institute SSEF. But from the very beginning, there has been evidence in the market of lower-quality rubies from Mozambique that have been heated with or without a flux (borax), resulting in healed fissures with residue, and in some cases heavily-fractured material that has been lead-glass filled.

In more recent years, an increasing number of rubies from Mozambique have come onto the market, after having undergone so-called "low-*empera*ure hea*ing" (below 1000 °C). Presumably, the aim of this treatment is to enhance the colour slightly, by reducing subtle purplish zones which are sometimes present in rubies from this location (Figure 1).

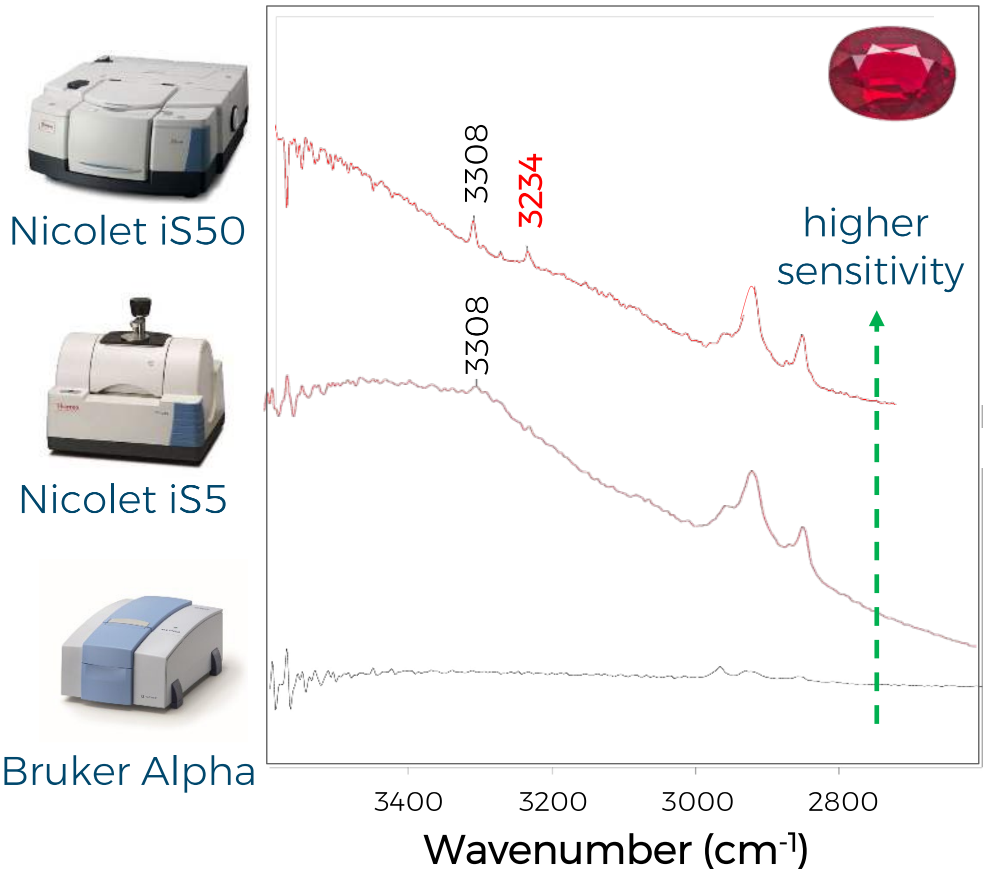
*Figure 1: Slightly purplish zone in ruby from Mozambique. Photo: M.S. Krzemnicki, SSEF*

SSEF press release in September 2018

**However, not all corundum will show such characteristic peak series!**

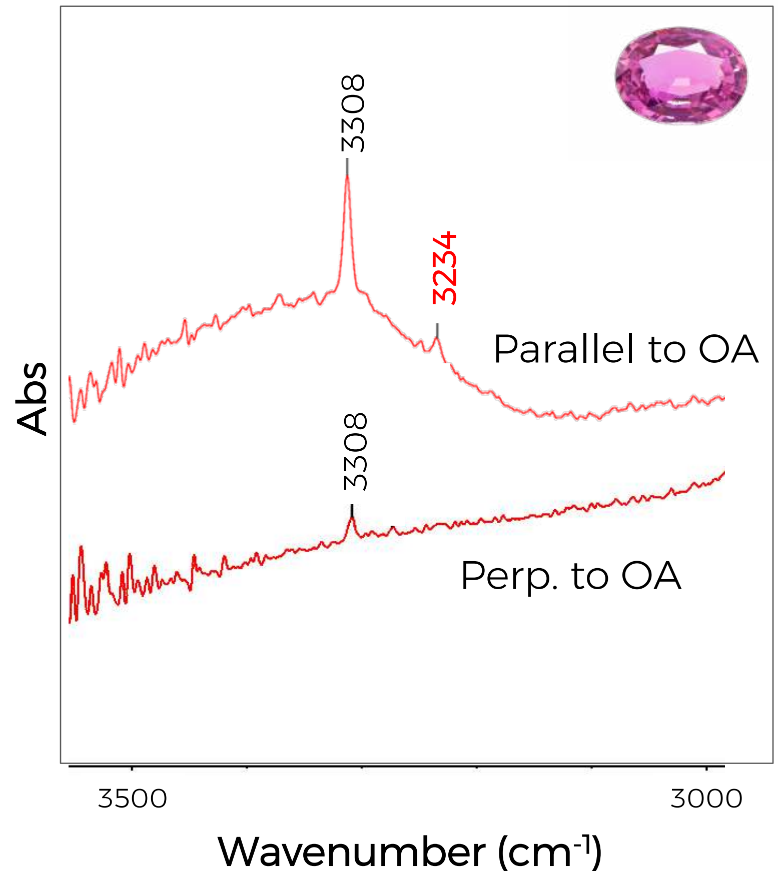
# Detection of Heat Treatment: Infrared Spectroscopy

## Effect of instrument sensitivity




FTIR spectra of same **heated** ruby with different FTIR instruments!

## Effect of sample orientation




FTIR spectra of same **heated** pink sapphire in different orientations!

# Detection of Heat Treatment: Infrared Spectroscopy

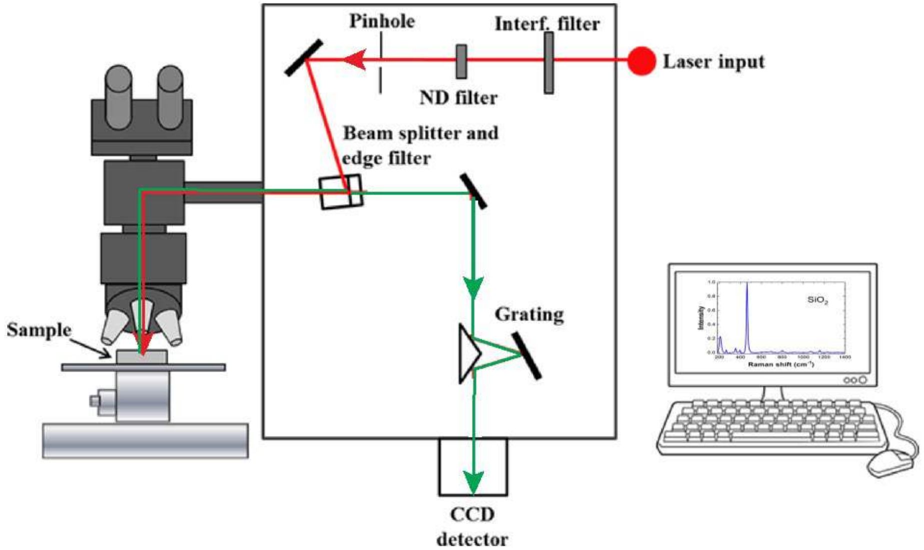
## Summarising: Infrared analyses

- FTIR spectra are very important for heat treatment detection.
- Specifically in cases in which no microscopic heating feature is present (e.g. low-T heat treatment).
- There is quite a large consensus in the gemmological scientific community and between the laboratories about key features of FTIR spectra indicating heating in corundum.
- A main issue remains the impact of anisotropy (sample orientation) on FTIR spectra and differences in instrumental sensitivity.

# Detection of Heat Treatment: Raman Spectroscopy

Raman micro-spectroscopy is a powerful tool to analyse a gemstone and its inclusions.

The laser beam focused through the microscope locally excites the molecules of the sample which results in a characteristic (vibrational) Raman spectrum of that sample/inclusion.

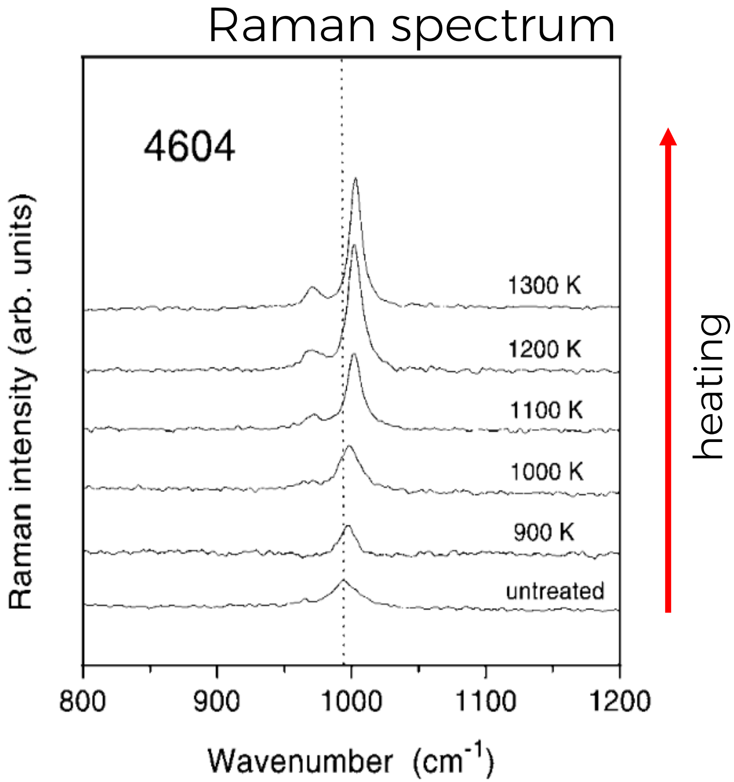

*Scheme (slightly modified) from Bonales et al. 2016*

# Detection of Heat Treatment: Raman Spectroscopy

Zircon inclusions may provide important information about heat treatment (and origin) of corundum.

*"Hot" pink sapphire from Ilakaka (Madagascar) containing many small zircon inclusions.*

Specifically useful for pink sapphires from Madagascar (Ilakaka).

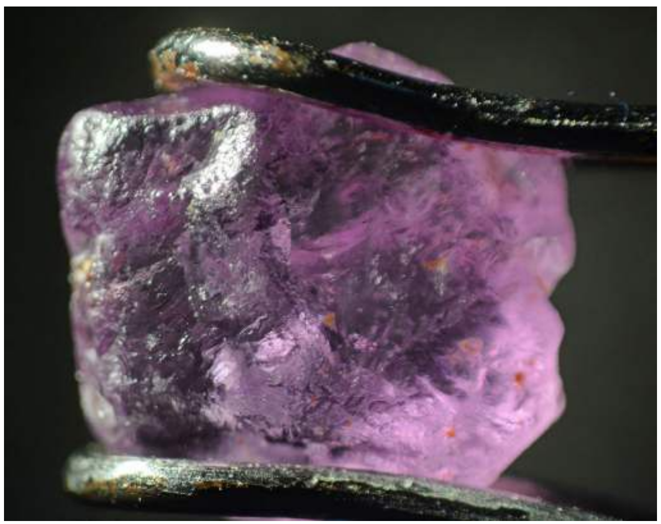


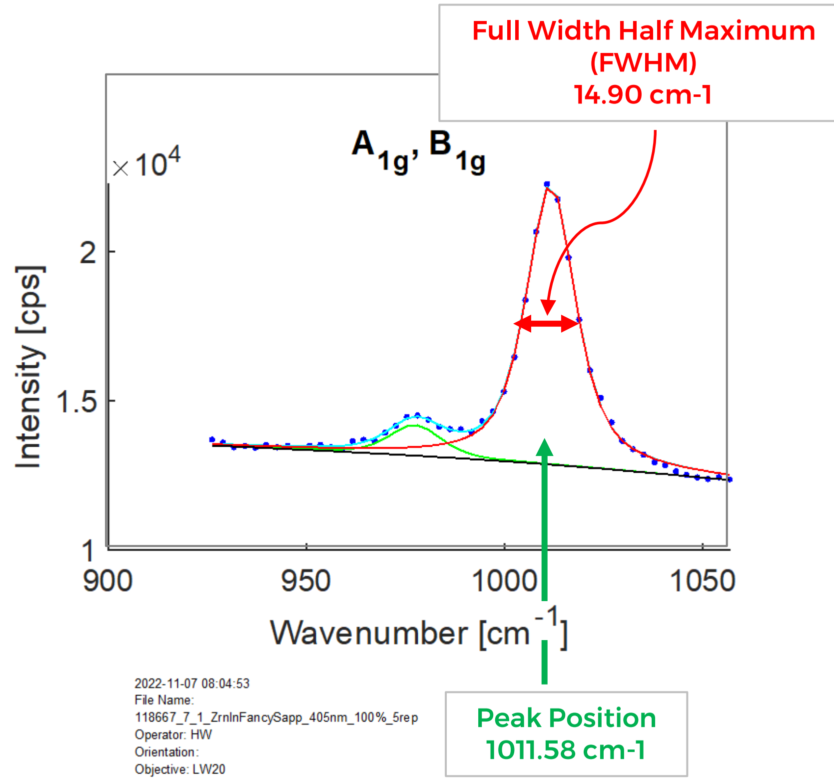

Spectra of zircon 4604 (dose $= 3.5 \times 10^{18}$ $\alpha$-events $g^{-1}$) annealed at different temperatures for one hour.

Zhang *et al. 2000*

# Detection of Heat Treatment: Raman Spectroscopy

Heating experiment of pink sapphire, Madagascar containing numerous tiny zircon inclusions!



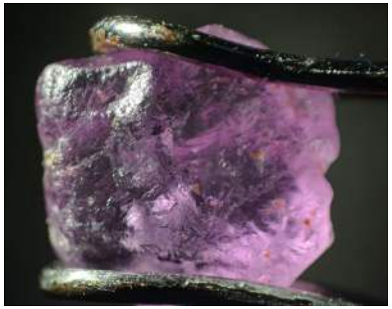



2022-11-07 08:04:53
File Name:
118667_7_1_ZrnInFancySapp_405nm_100%_5rep
Operator: HW
Orientation:
Objective: LW20
Repetition:
Zircon Type:
Calib on Si wafer: Yes
Calib Pos: 519.79 cm$^{-1}$
Calib FWHM: 6.26 cm$^{-1}$
IntRatio 974/439: 0.27 [0-0.5]
$A_{1g}$ (974) Pos: 977.35 cm$^{-1}$
$A_{1g}$ (974) FWHM: 15.46 cm$^{-1}$
$A_{1g}$ (974) Int: 1034.03 cm$^{-1}$
$B_{1g}$ (1008) Pos: 1011.58 cm$^{-1}$
$B_{1g}$ (1008) FWHM: 14.90 cm$^{-1}$
$B_{1g}$ (1008) Int: 9411.20 cps

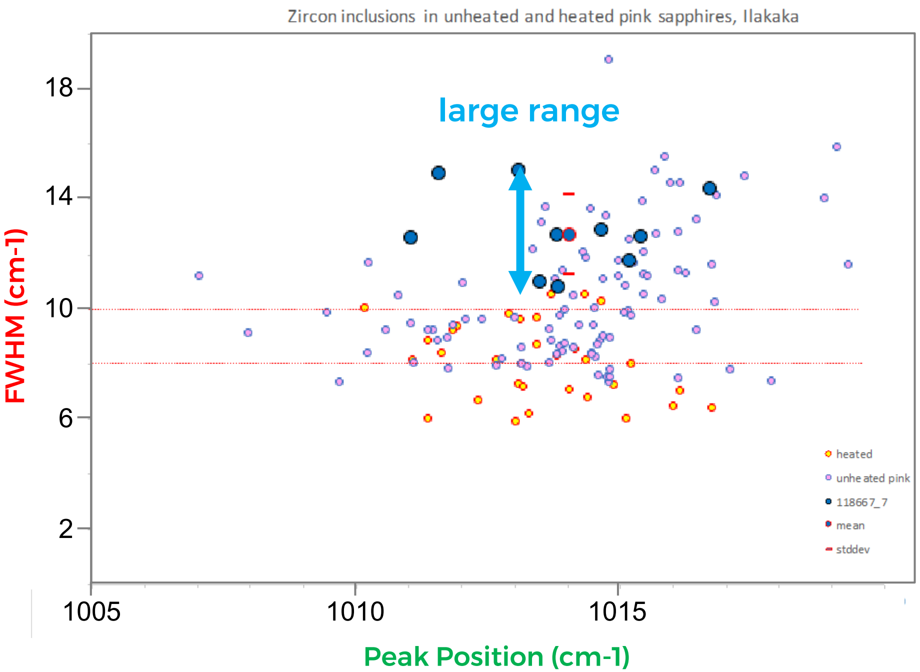
In-house developed automated peak calculation (Dr Hao Wang).

# Detection of Heat Treatment: Raman Spectroscopy

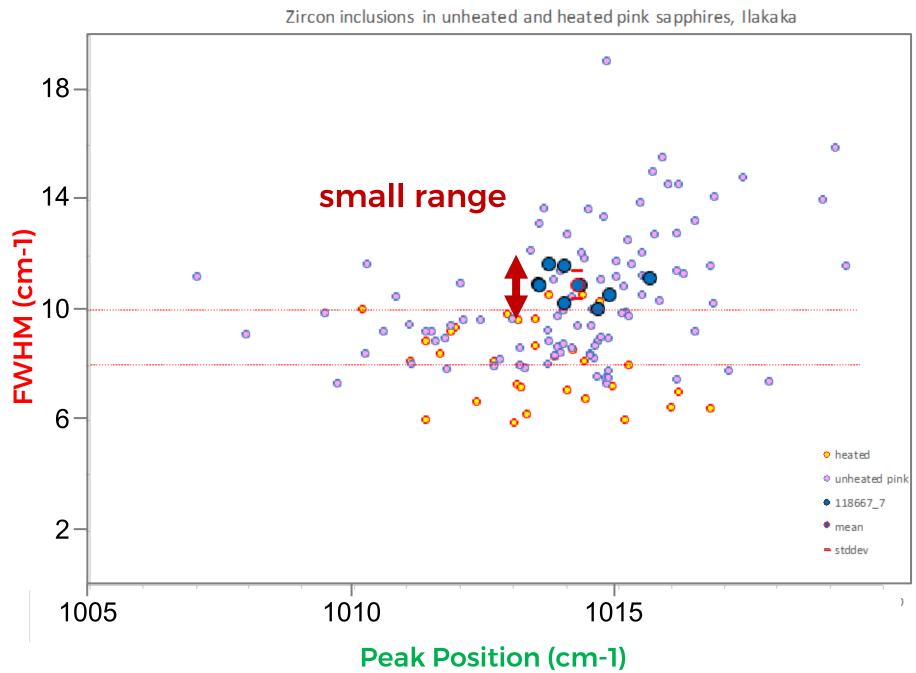
Heated in oxidizing conditions at 1000° C
for 1 hour (peak T).
Analysed before and after !



Peak position vs Peak width (FWHM) Diagrams



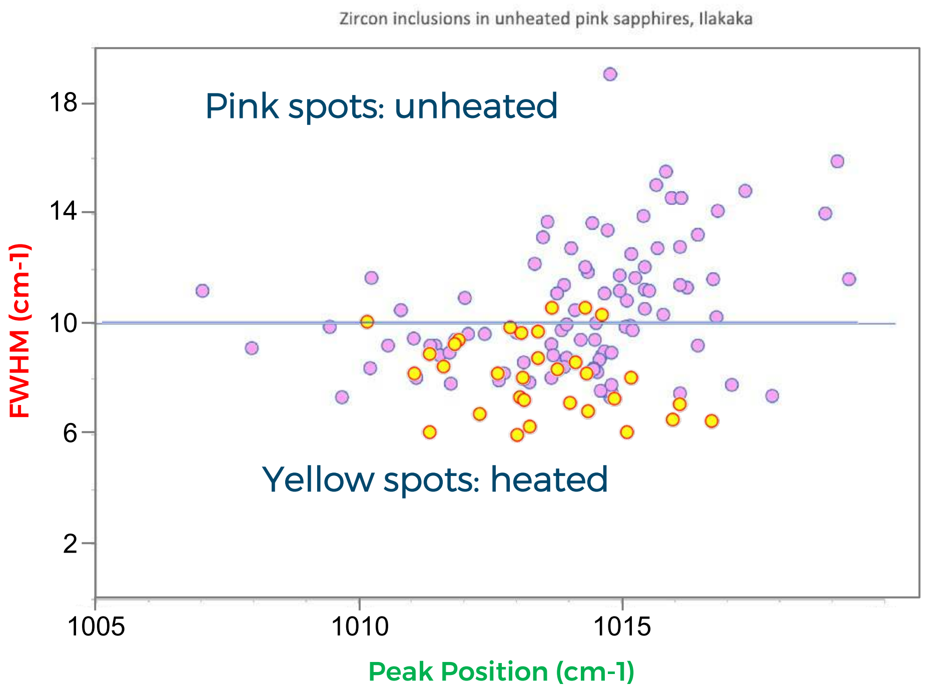

FWHM of zircons before




FWHM of zircons after heating

# Detection of Heat Treatment: Raman Spectroscopy

Peak position vs Peak width (FWHM) diagrams





**Zircon inclusions in unheated pink sapphires from Ilakaka, Madagascar: A Raman spectroscopic study**

**M.S. Krzemnicki, P. Lefèvre, W. Zhou, H.A.O. Wang**
**Swiss Gemmological Institute SSEF**
**gemlab@ssef.ch**

Since its discovery in 1998, the secondary gem deposit of Ilakaka, southwestern Madagascar has produced a large number of outstanding stones for the gem trade, notably sapphires and fancy sapphires in a wide range of colours (Milisenda et al. 2001). Until today, pink sapphires from Ilakaka are found in great numbers in the trade, often characterised by an outstanding quality and a pastel pink to vivid pink ("hot pink") colour.

Interestingly, pink sapphires from Ilakaka commonly contain numerous rounded zircon inclusions, sometimes even clustered in aggregates (Figure 1). Zircon is found in corundum from many different geological settings and geographic origins and may provide crucial information for gem testing, both, regarding heat treatment (Wang et al. 2006, Krzemnicki 2010, Saeseaw et al. 2020) and origin determination (Xu & Krzemnicki 2021).

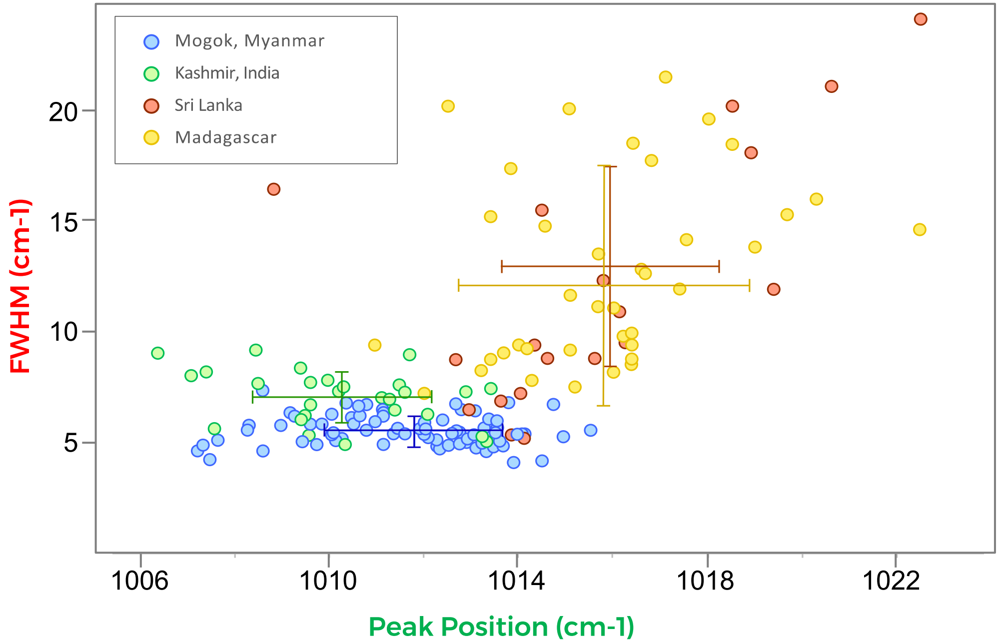
The Raman analysis of zircon inclusions in pink sapphires from Ilakaka (Madagascar) is widely used in gem labs as a routine test as it may provide supporting analytical evidence of a heat treatment. In this study, we focus on Raman spectra of zircon inclusions in unheated pink to purplish pink sapphires from Ilakaka to better characterise and understand the range and variability of the $SiO_4$-related bandwidths. More than 100 zircon inclusions in 28 samples (rough and cut) from the SSEF research collection were analysed using an InVia Renishaw Raman microprobe coupled with a 514 nm argon-ion laser. In accordance with literature (Nasdala et al. 1995, Wang et al. 2006, Saeseaw et al. 2020) we focussed on the main Raman peak u3 ($SiO_4$ anti-symmetrical stretching mode) of zircon at about 1010 $cm^{-1}$ as

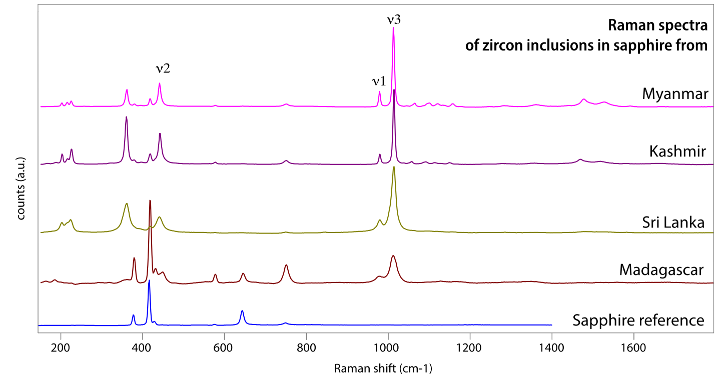
Krzemnicki et al. 2021

However, overlapping FWHM ranges of unheated and heated pink sapphires from Madagascar (Ilakaka) remain a challenge for heat treatment detection.

# Detection of Heat Treatment: Raman Spectroscopy

The influence of the geographic origin




Figures:
Xu & Krzemnicki 2021

FWHM range criterion to detect heat treatment is not applicable for corundum from many important gem deposits (e.g. Myanmar, Kashmir, or Basaltic origin).

# Detection of Heat Treatment: Raman Spectroscopy

An additional approach:
Phase transformations of hydroxides
Diaspore ($\alpha$-AlOOH) and Goethite ($\alpha$-FeOOH)

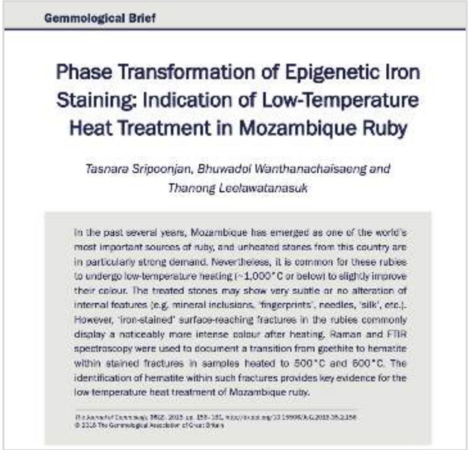
Transformation of goethite to hematite.
from Koivula 2013

2 diaspore $\xrightarrow{\text{about 500°C}}$ 1 corundum + water

$2\ AlOOH \rightarrow Al_2O_3 + H_2O$

2 goethite $\xrightarrow{\text{about 350°C}}$ 1 hematite + water

$2\ FeOOH \rightarrow Fe_2O_3 + H_2O$



Gemmological Brief

Phase Transformation of Epigenetic Iron Staining: Indication of Low-Temperature Heat Treatment in Mozambique Ruby

*Tasnara Sripoonjan, Bhuwadol Wanthanachaisaeng and Thanong Leelawatanasuk*

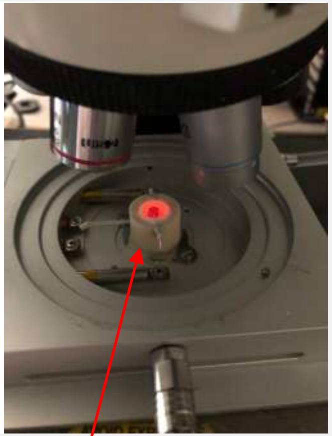
In the past several years, Mozambique has emerged as one of the world's most important sources of ruby, and unheated stones from this country are in particularly strong demand. Nevertheless, it is common for these rubies to undergo low-temperature heating (~1,000°C or below) to slightly improve their colour. The treated stones may show very subtle or no alteration of internal features (e.g. mineral inclusions, 'fingerprints', needles, 'silk', etc.). However, 'iron-stained' surface-reaching fractures in the rubies commonly display a noticeably more intense colour after heating. Raman and FTIR spectroscopy were used to document a transition from goethite to hematite within stained fractures in samples heated to 500°C and 600°C. The identification of hematite within such fractures provides key evidence for the low-temperature heat treatment of Mozambique ruby.

Sripoonjan et al. 2016

These are so-called **dehydration reactions** which occur when heating up these hydroxides (diaspore, goethite).

# Heating Experiment

**Heating stage Linkam TS 1200**
- Coupled with Raman system for in-situ measurements



Glowing ruby at 700 °C

Step-wise heating,
$T_{max}$ per step kept for 4 minutes only

**Electric muffle furnace Nabotherm LHT 18**
- Heating similar to gem trade

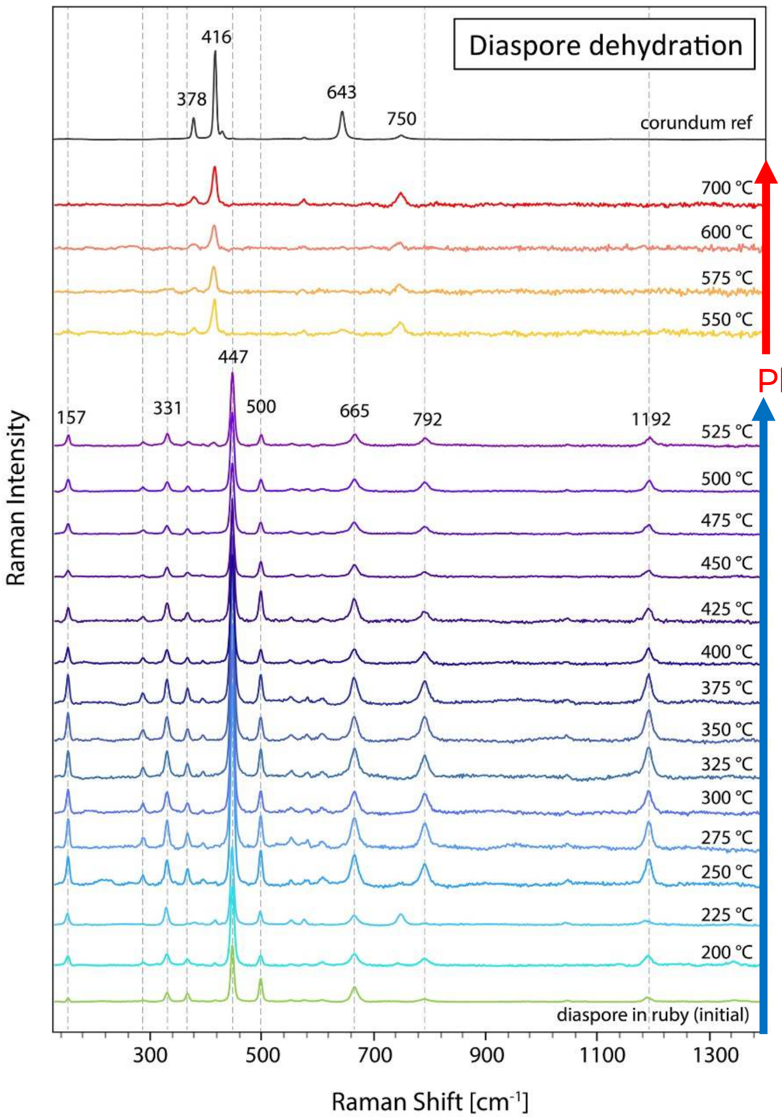
Step-wise heating,
$T_{max}$ per step kept for 1 hour

Heating in air, step-by-step heating, Raman spectra only after cooling down

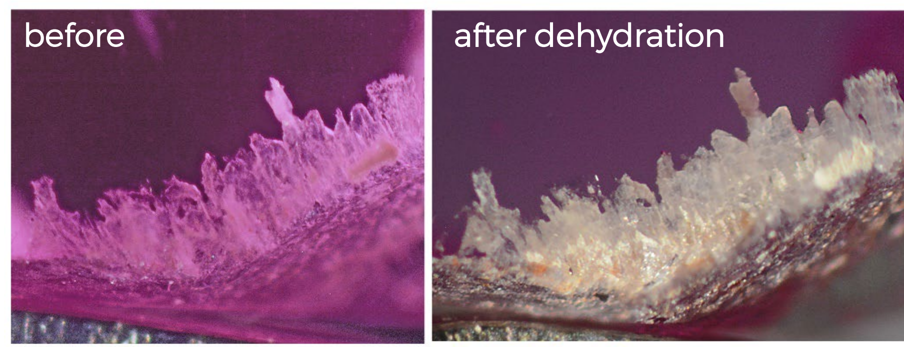
# Heating Experiment: Diaspore to Corundum

Sample 120993_6
Diaspore in Burmese ruby (Mogok)

Experiment setup:
Linkam heating stage




dotted vertical lines: main diaspore peaks

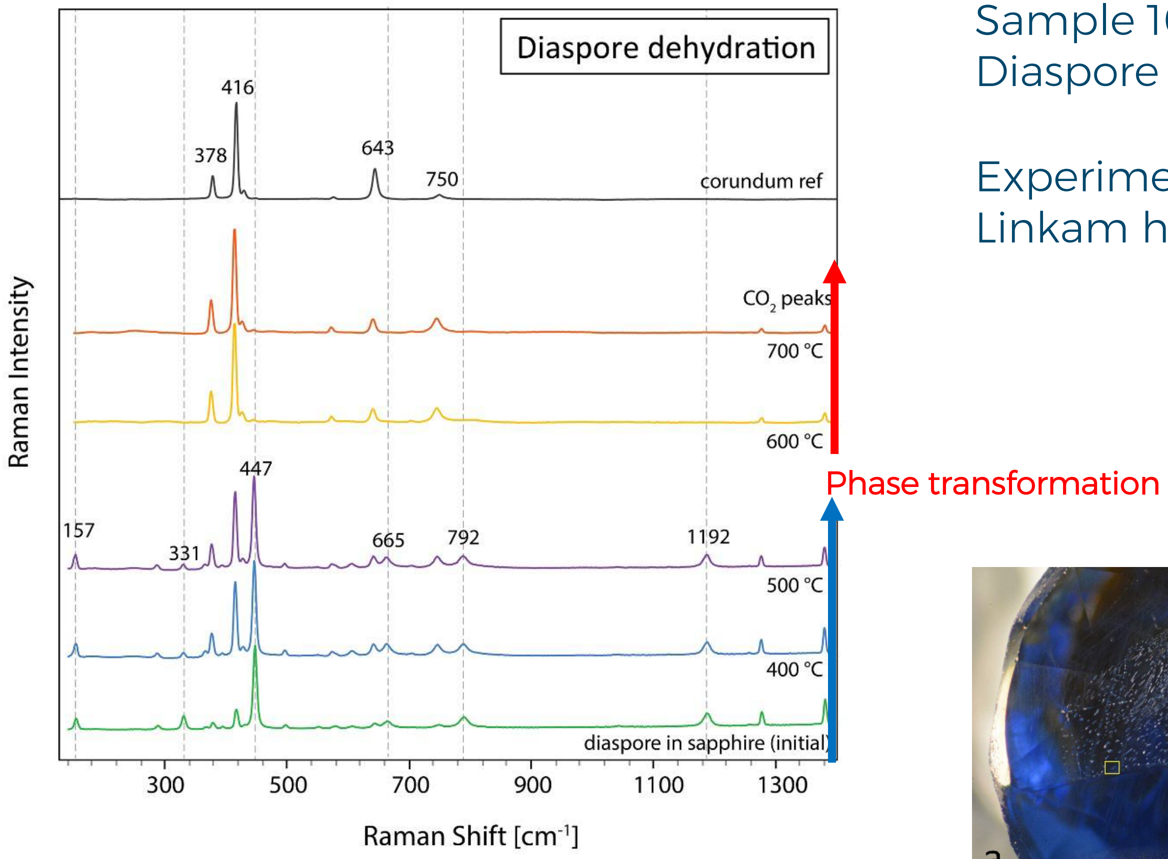



Diaspore in ruby (image width 2mm).

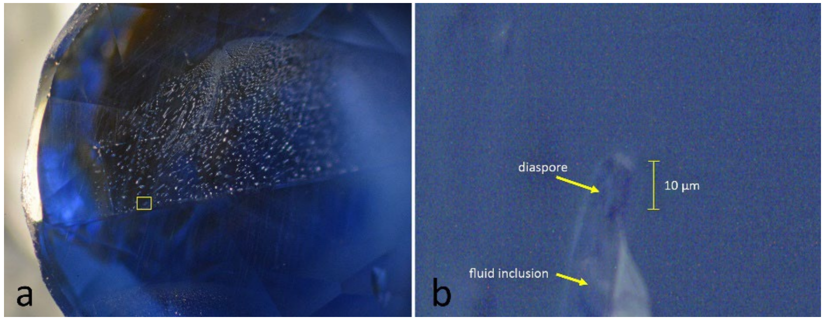
# Heating Experiment: Diaspore to Corundum

Sample 106424_21
Diaspore in Burmese sapphire (Mogok)

Experiment setup:
Linkam heating stage

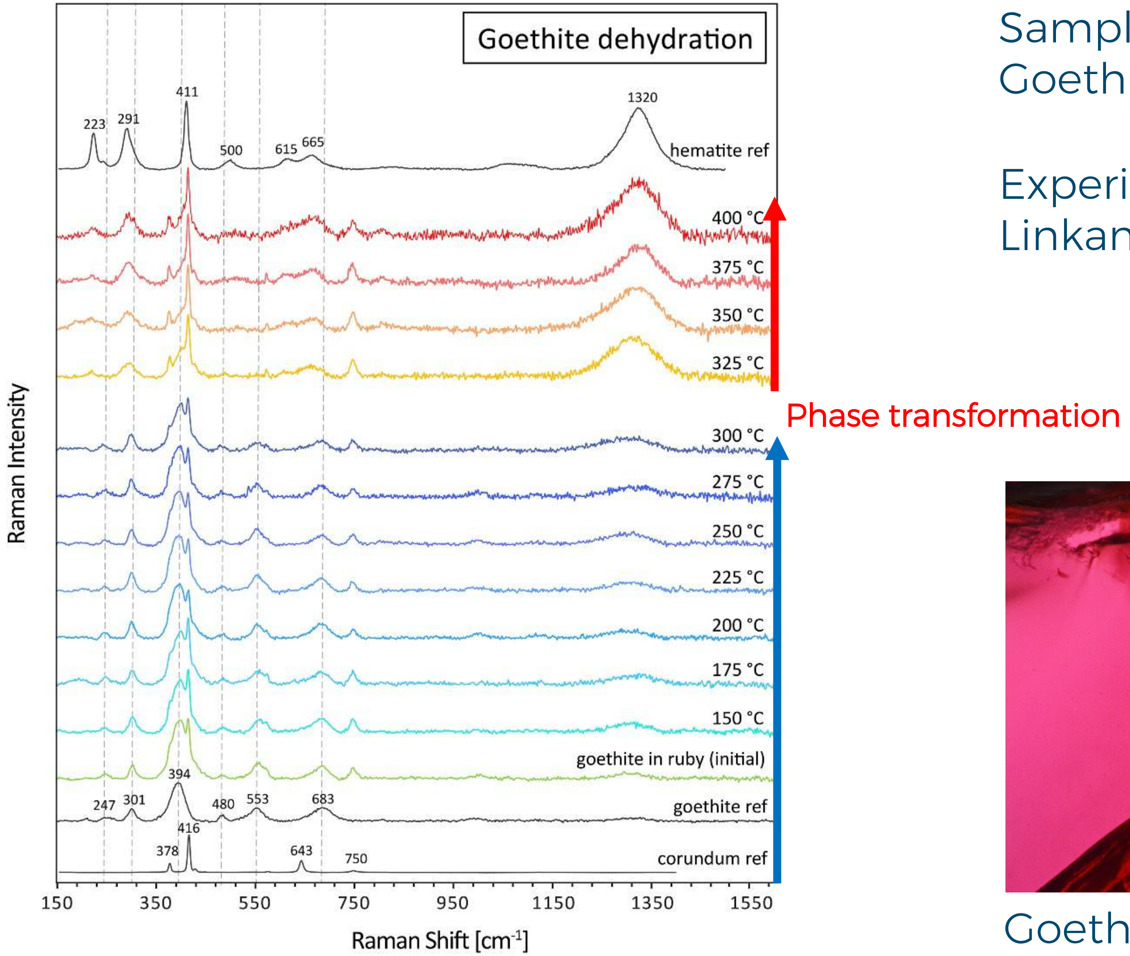



dotted vertical lines: main diaspore peaks



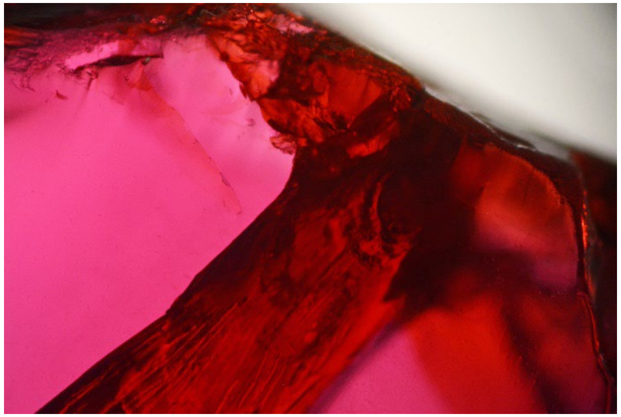

Diaspore in fluid inclusion in sapphire (approx. 10 µm).

# Heating Experiment: Goethite to Hematite




Sample 85933_C3
Goethite in Mozambique ruby

Experiment setup:
Linkam heating stage

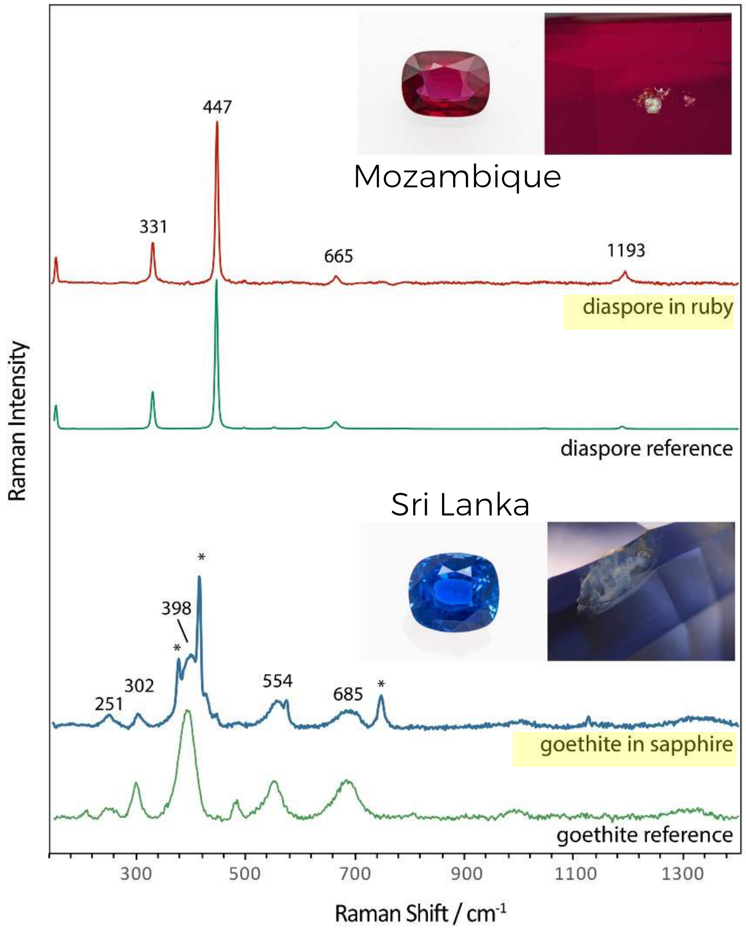


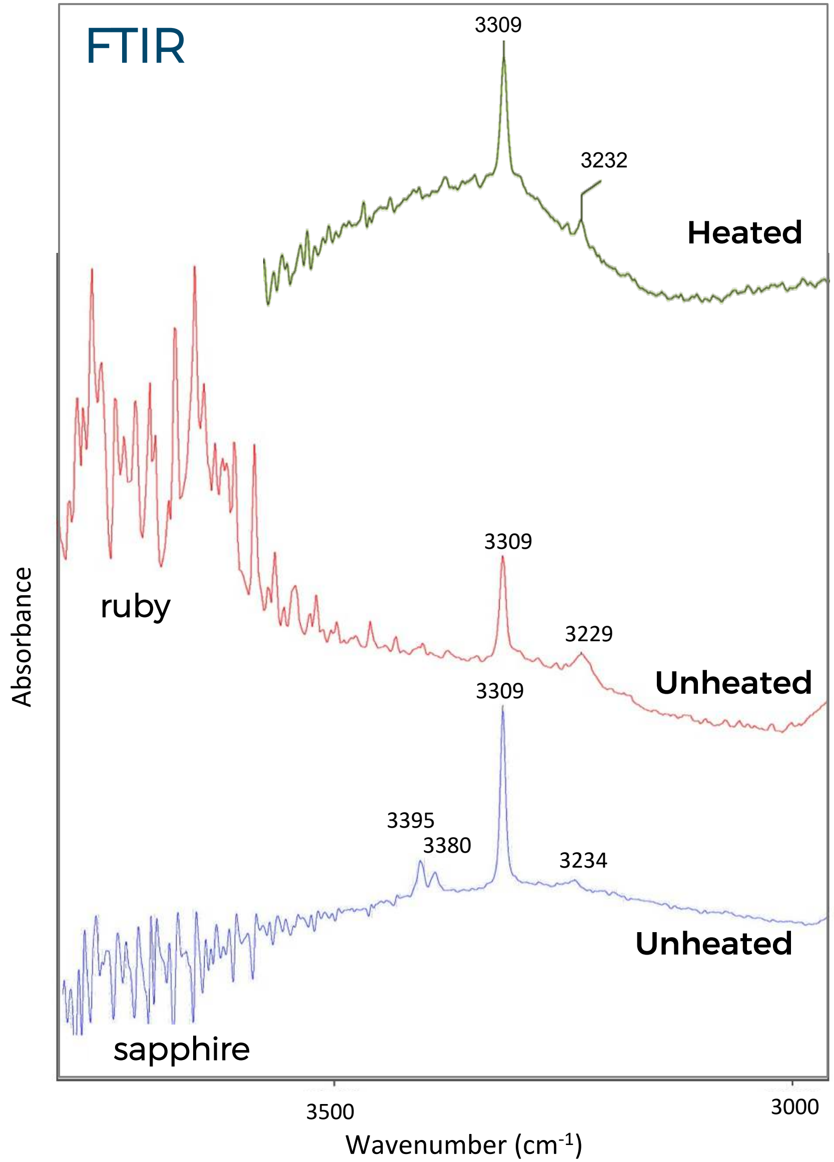
Goethite in fissure in ruby

dotted vertical lines: main goethite peaks

# Real Cases

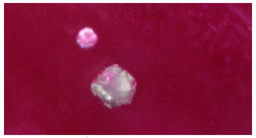
## Raman

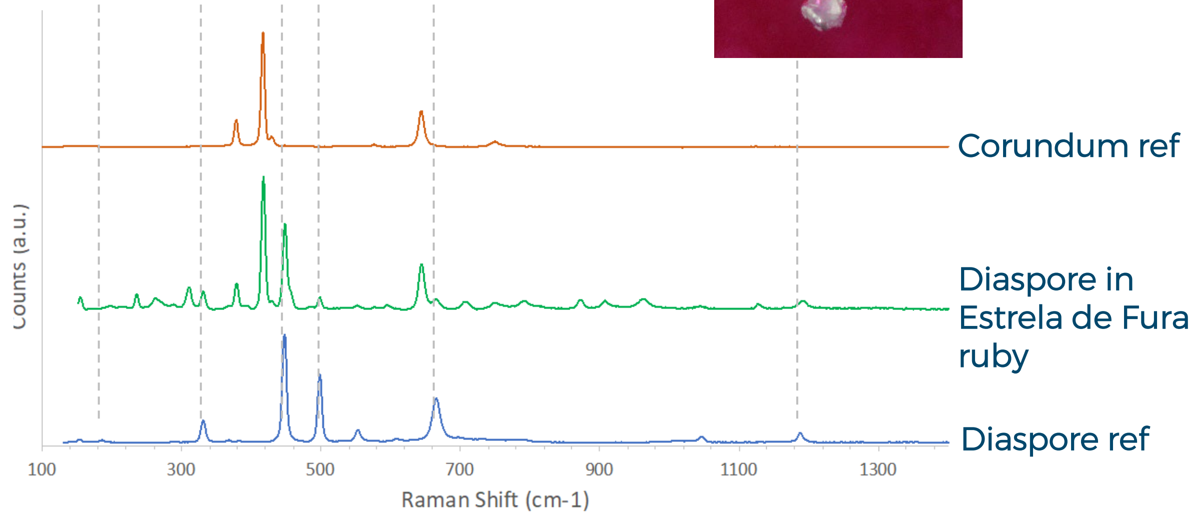



Raman spectroscopy of diaspore and goethite inclusions prove that the ruby and sapphire are unheated, although their infrared spectra is similar to heated corundum!

# Real Cases






Diaspore detected in fluid inclusion !

Estrela de Fura 55.22 ct

Sold at Sotheby's auction in June 2023 for record $34.8 million.

from Sotheby's International

# Detection of Heat Treatment: Raman Spectroscopy

Summarising: Raman analyses

- Raman spectroscopy on inclusions is a **very promising** tool to separate unheated corundum from low-temperature heated corundum.
- The zircon peak-width criterion (FWHM) is challenging (specifically to detect low-temperature heated corundum) and cannot be applied on corundum from certain (geologically young) gem deposits.
- **However, the phase transformations of diaspore and goethite are key to separate unheated corundum from low-temperature heated stones.**
- Our **experiments** confirm that diaspore and goethite transform (dehydrate) at about 325 °C (goethite to hematite) and about 550 °C (diaspore to corundum).
- The presence of diaspore and/or goethite is a **clear indication**, that a corundum is **not heated**, even in cases when FTIR may reveal peaks which could be (mis)interpreted as related to heating.

# Detection of Heat Treatment: Raman Spectroscopy

## Summarising: Raman analyses

minerals

MDPI

check for updates

**Citation:** Krzemnicki, M.S.; Lefèvre, P.; Zhou, W.; Braun, J.; Spiekermann, G. Dehydration of Diaspore and Goethite during Low-Temperature

https://doi.org/10.3390/ min13121557

# Take Home Messages

- Detection of low-temperature heating of corundum is **challenging**.
- The best is to use a **combined approach** ('classic' and spectroscopic methods), although microscopic features indicating heating may not be present.
- **Infrared (FTIR)** and **Raman spectroscopy** are key for separating unheated from heated stones.
- Scientific research in gemmology **constantly evolves**, actually parallel to the development of new treatment processes and the discovery of new deposits.
- Consequently, **new findings** may lead in certain cases also to **new conclusions**, similar to any other branch of science.
- Gemmological labs **exchange their new findings** about treatment detection, by
  - publication of results in scientific journals
  - at gemmological conferences
  - in gemmological working groups (e.g. LMHC)
  - by inter-lab discussions
- By this we aim to **harmonise results as much** as possible and as such to support the gemstone trade and public with our expertise.

# Thank you for your attention

Corroded calcite inclusions in an unheated Burmese ruby from Mogok.

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