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How to get the Blues out of the Pink:

Detection of low-Temperature treatment of pink sapphires

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Think pink

...a fashion trend

What is pink ?

- ruby ?

- pink sapphire ?

- purple sapphire ?

The source

Map and Photo © R.W. Hughes

Ilakaka in Madagascar and Tunduru in Tanzania are important sources for sapphires in all colours, especially pink!

Pink sapphires from Madagascar

The heat treatment of corundum

Difficult to detect with the microscope

Heating

Low temperature heating (<1000 °C),
e.g. purplish sapphires become pink when heated in oxidising conditions
effect: colour shift, blue colour component is reduced

Heating > 1000 °C, e.g. for geuda corundum, rubies from Thailand
effect: colour modification, reducing visibility of inclusions

Heating with flux

Heating with high refractive glass flux, e.g. lead glass
effect: significant enhancement of transparency and colour (and stability)

Heating with borax flux, e.g. rubies from Mong Hsu (Burma)
effect: significant enhancement of transparency and colour

Heating with diffusion

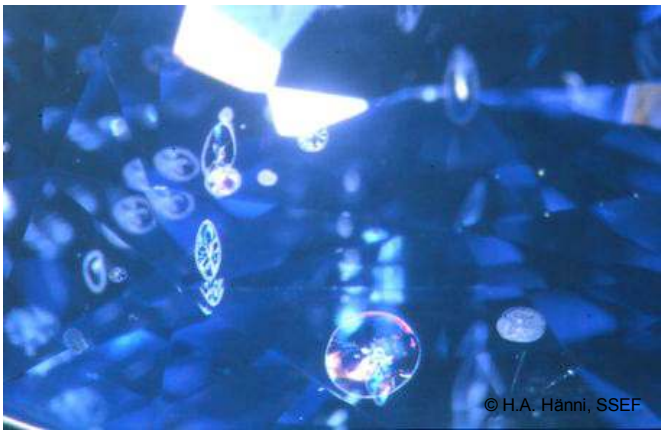
Heating with chromium diffusion (shallow)
effect: creation of shallow colour zone

Heating with beryllium diffusion (lattice, bulk), e.g. corundum from Songea
effect: significant colour modification

The heat treatment of corundum

Microscopic features of heated corundum

Characteristic disc-shaped „atoll islands“:
Features of inclusions which were melting and exploded during the heating!



Microscopic features of heated corundum

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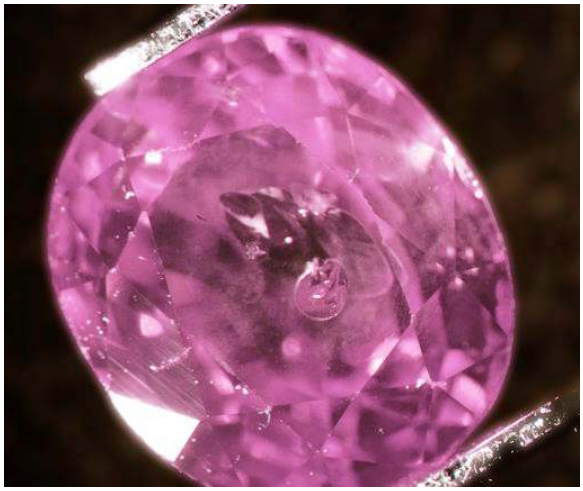
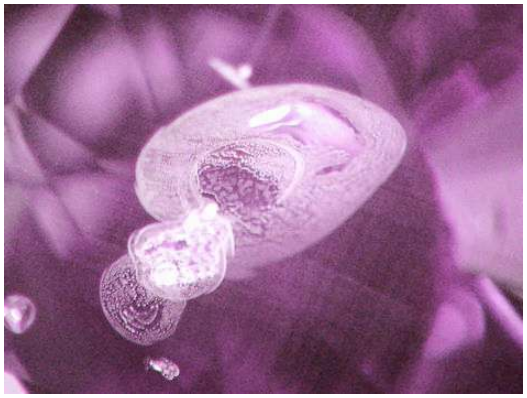
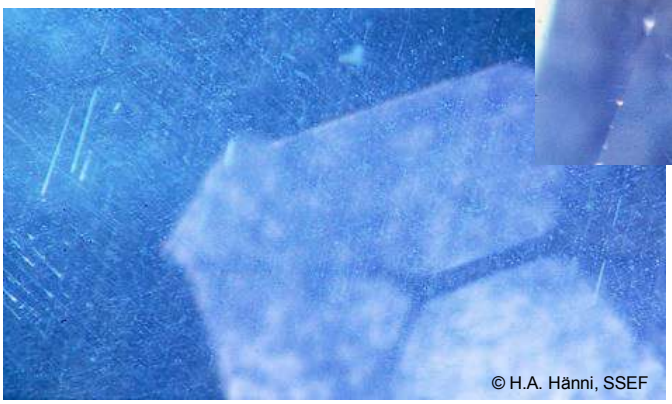




Microscopic features of heated corundum

The (partial) dissolution of rutile needles occurs after heating above approx. 1200 °C.

Below that temperature, the rutile needles remain unaltered!



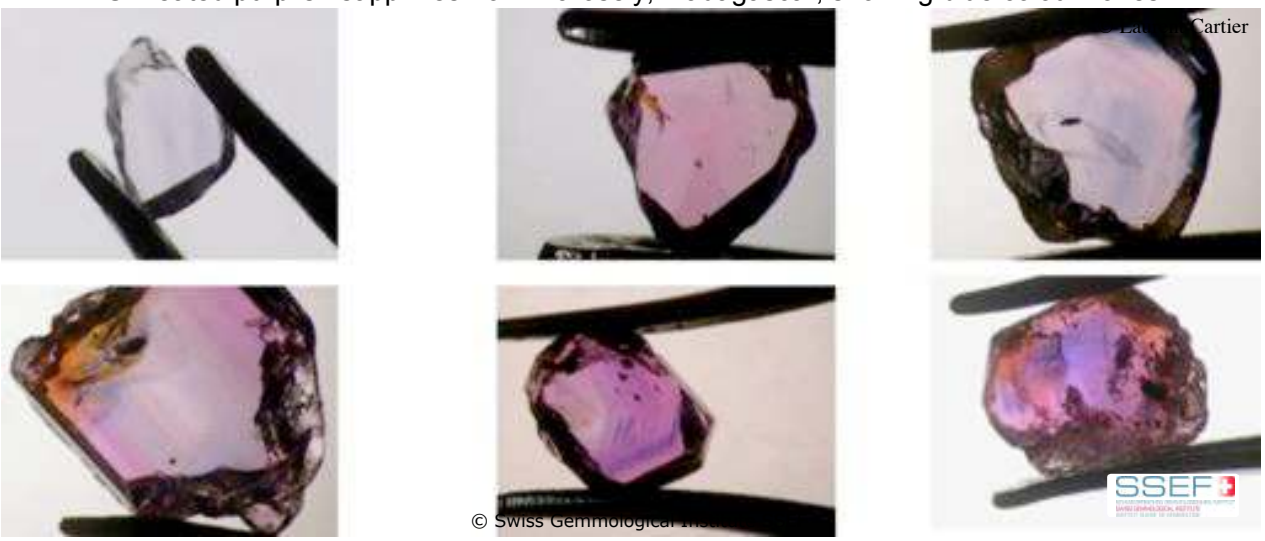
The presence of fine rutile needles does **not** mean that the stone is **unheated**!

The starting point

- The lower the heating temperature,
  the more difficult is the detection by microscope.

- Colour enhancements of corundum may already occur at approx. 600 °C.

Unheated purplish sapphires from Marosely, Madagascar, showing blue colour zones.



The starting point

Perfect would be:

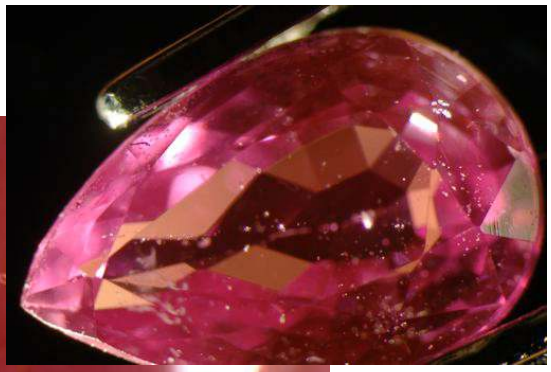
- A criterion which can be measured / analysed
  (e.g. with Raman-microspectrometry on inclusions)

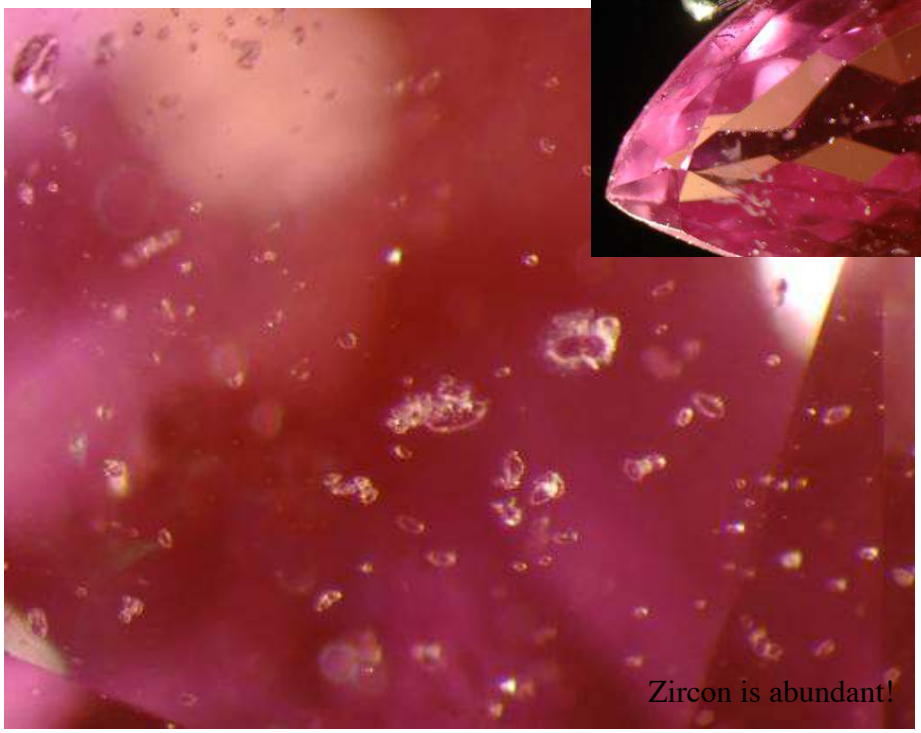
- An inclusion hich changes in relation to the heating temperature

- An inclusion which is found very often in corundum

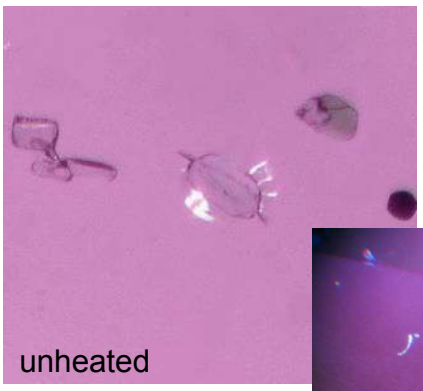
Zircon

Zircon in pink sapphire

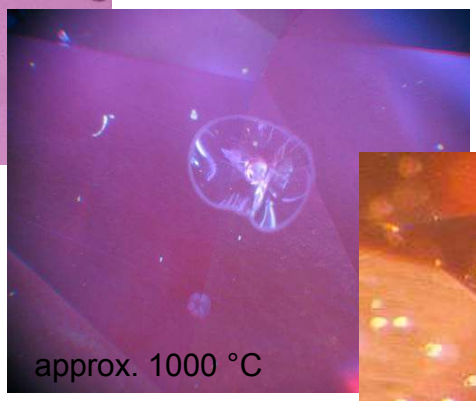


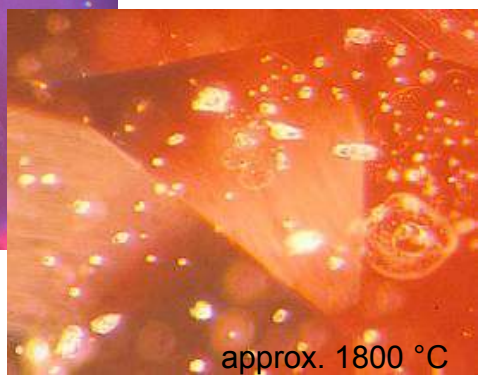


Zircon in pink sapphire

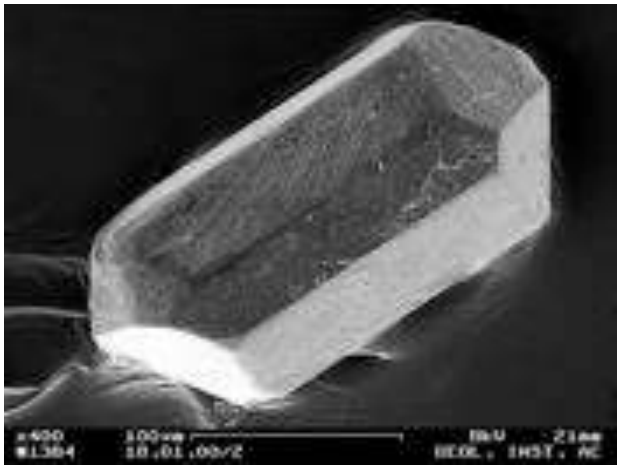


Zircon inclusions change their appearance with increasing heating temperature!





Zircon

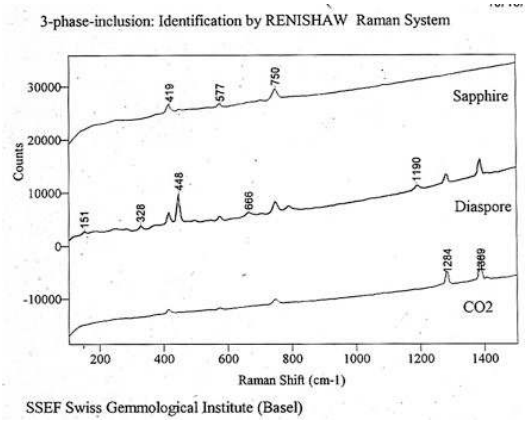


Zircon $ZrSiO_4$ often contains small amounts of radioactive elements such as thorium and uranium.

The radiation which is released during the decay of these radioactive trace elements is damaging locally the crystal structure of the zircon which becomes metamict (isotropy, RI and SG are reduced, volume increased).

Metamict zircon crystals can be „repaired“ by heating; the deformed structure is adjusted!

Raman-microspectrometry



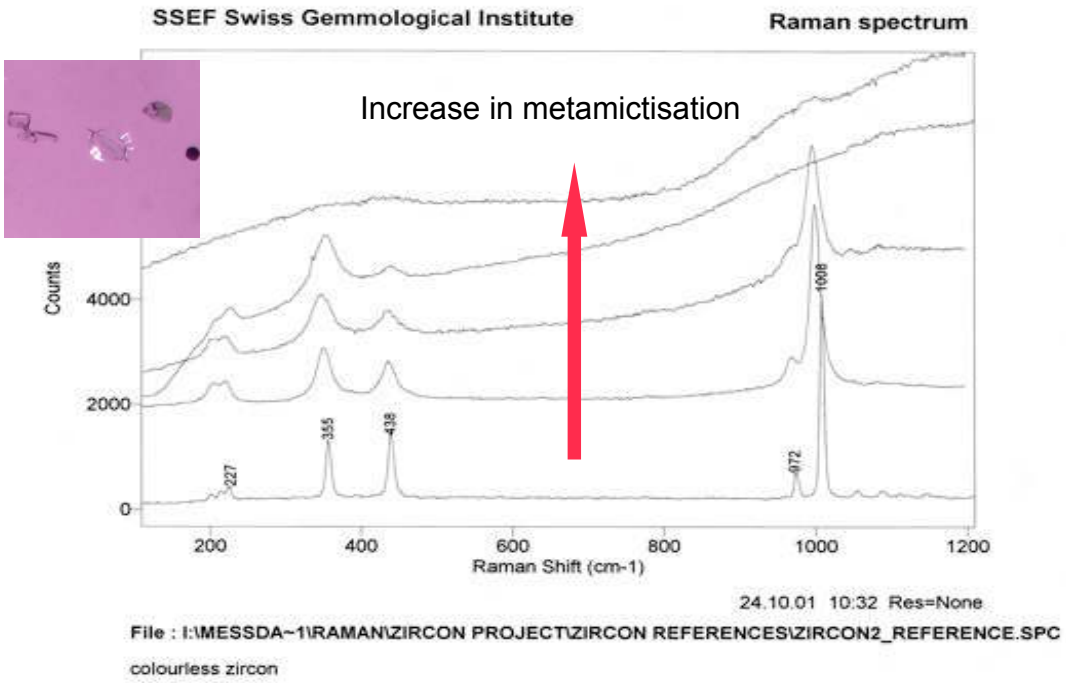
The molecules of a substance (solid/liquid/gas) are excited with a laser. The Raman microspectrometer registers these vibrational emissions.

Each substance has its characteristic molecular structure, thus shows also a characteristic Raman spectrum (RRUFF-Project)

The confocal laser beam enables the analysis of a tiny volume on the surface or even within a transparent material.

Identification is possible by comparing the registered Raman spectrum with a database.

Raman spectra of zircon



Experiment 1: Heating of zircon

Before heating | **After heating**

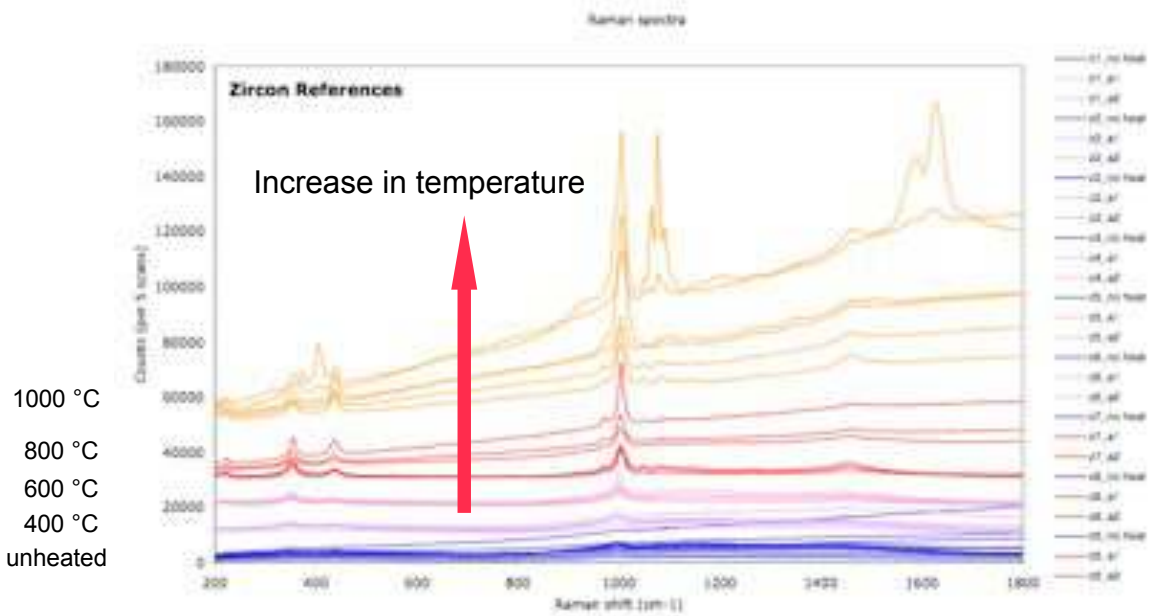
A: 400 °C

B: 600 °C

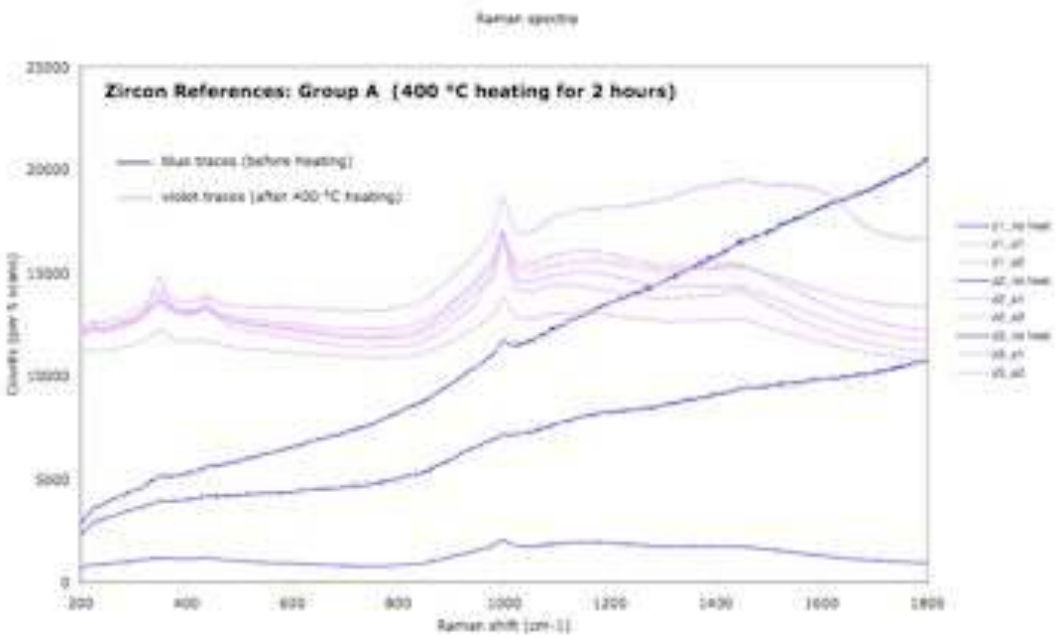
C: 800 °C

D: 1000 °C

Heating of zircon



Heating of zircon



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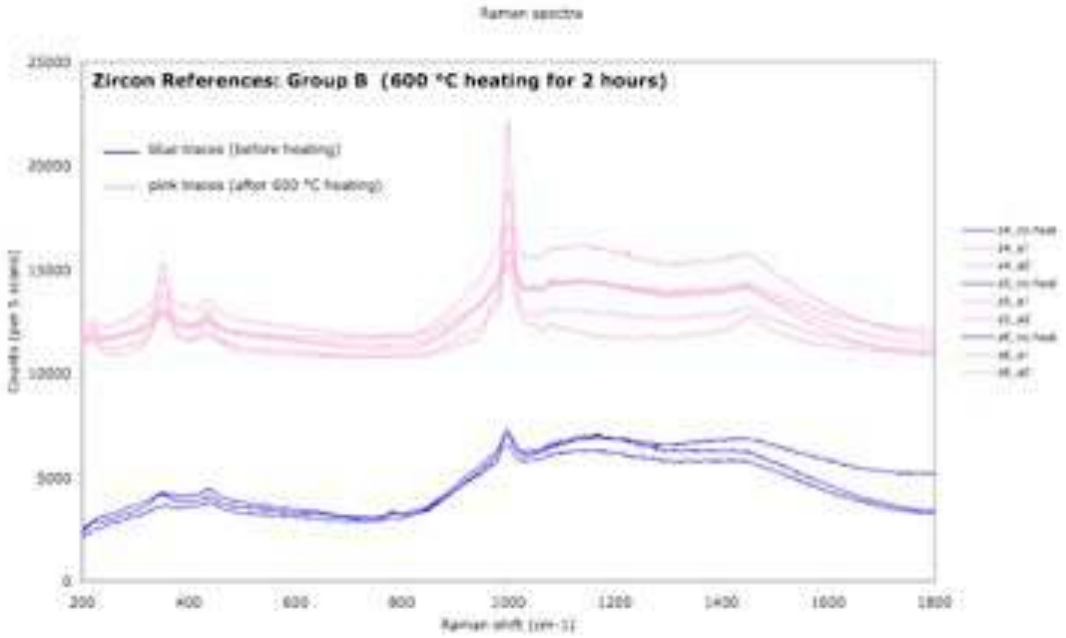
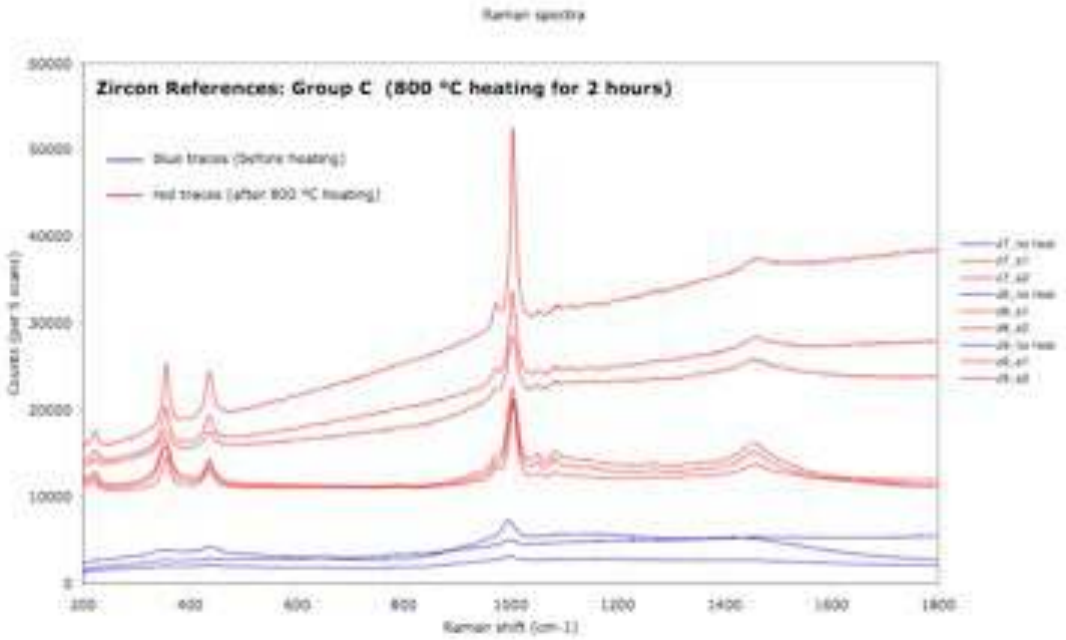
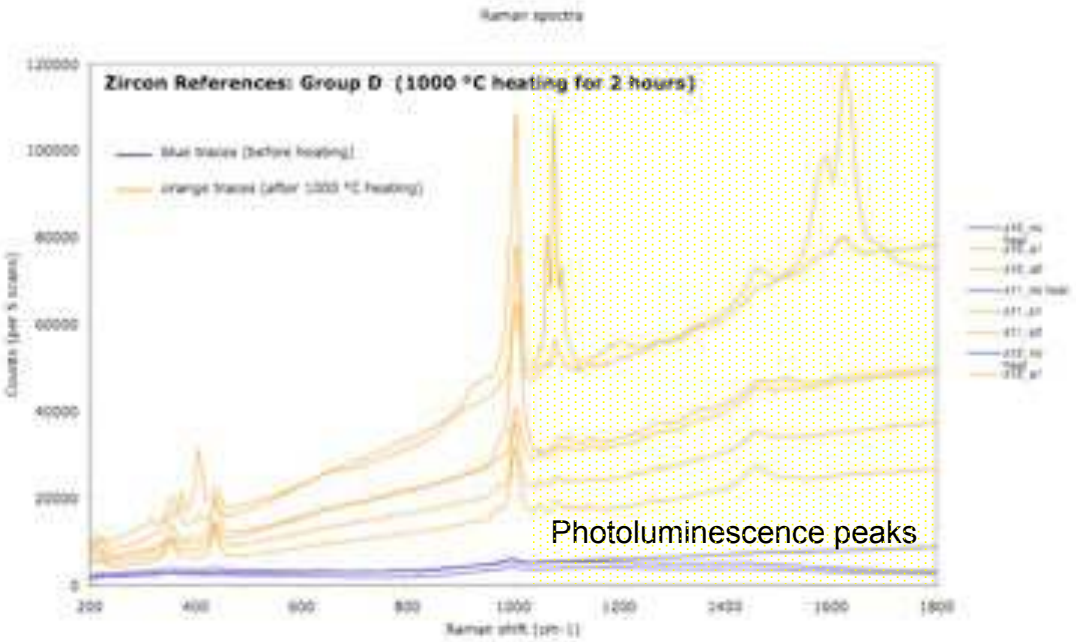


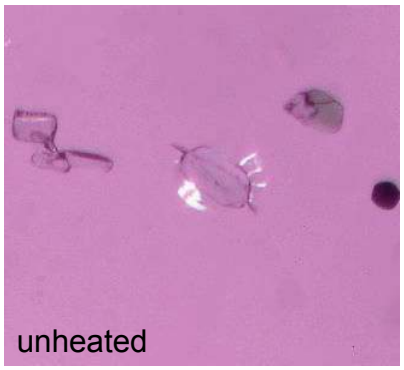
Heating of zircon



Heating of zircon



Zircon



Characteristic „Insect-wings“ (tension cracks) around a partially metamict zircon inclusion in a pink sapphire.

Experiment 2: Heating of pink sapphire

A total of 25 corundum were heated at oxidising conditions:

Group A: 400 °C for 2 hours

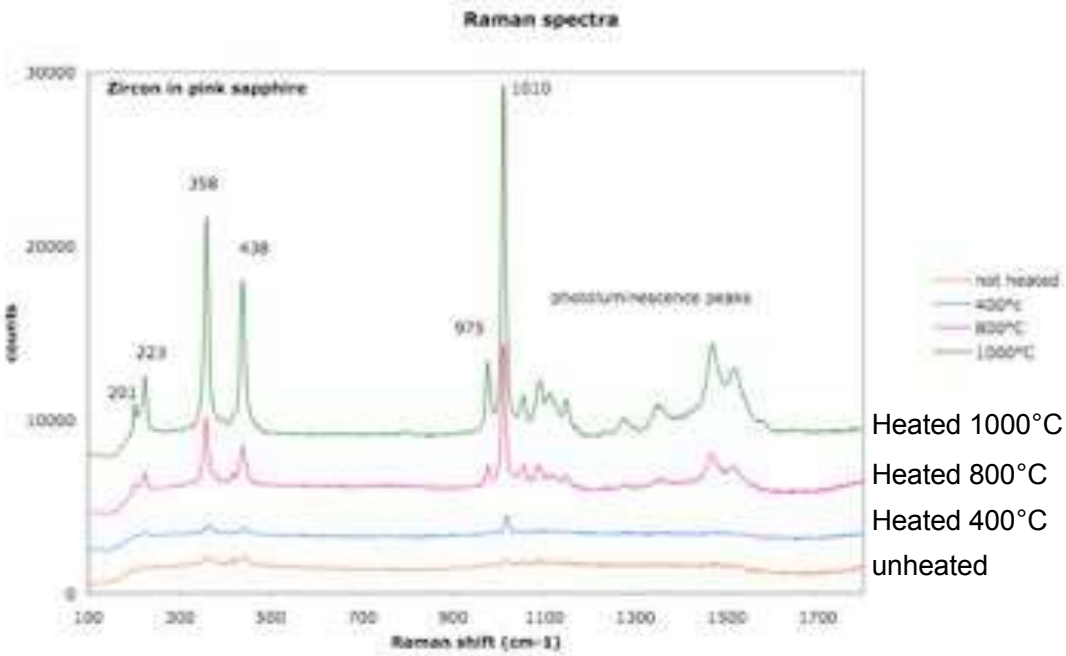
Group B: 600 °C for 2 hours

Group C: 800 °C for 2 hours

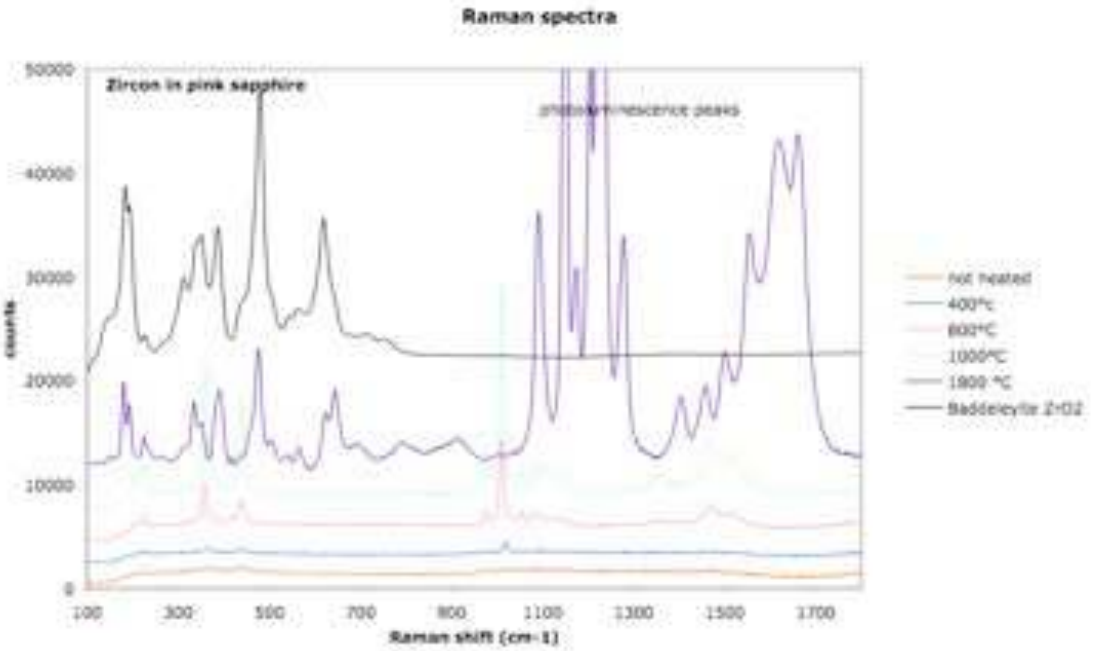
Group D: 1000 °C for 2 hours

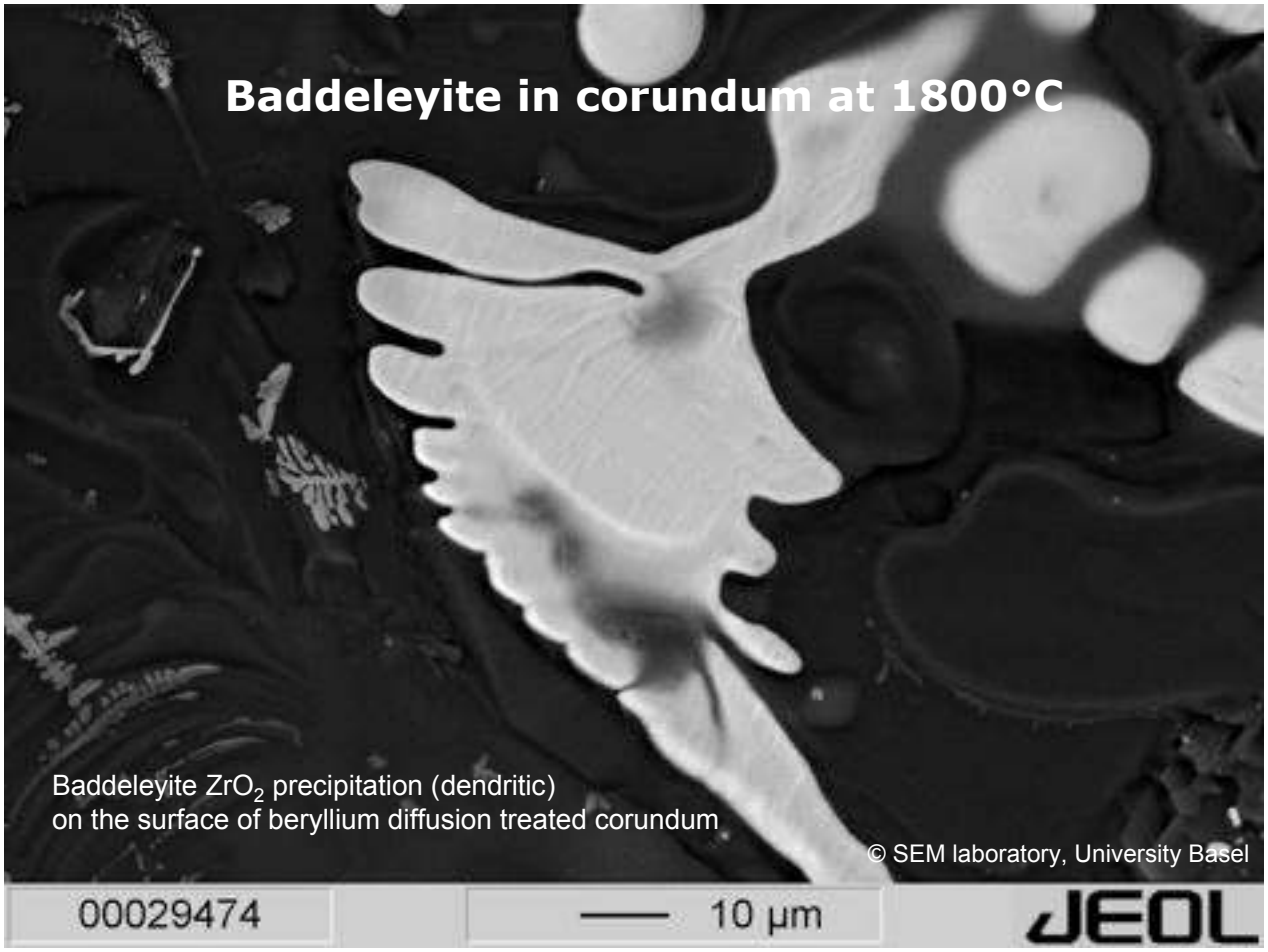
All specimens were analysed with the Raman before and after heating!

Raman spectra of zircon inclusions (unheated to 1000°C heated)

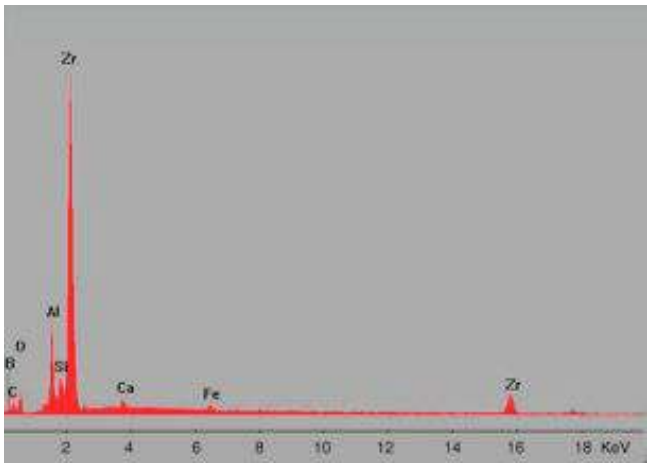


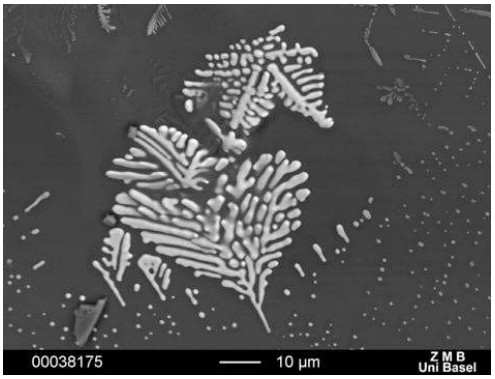
What happens at 1800°C

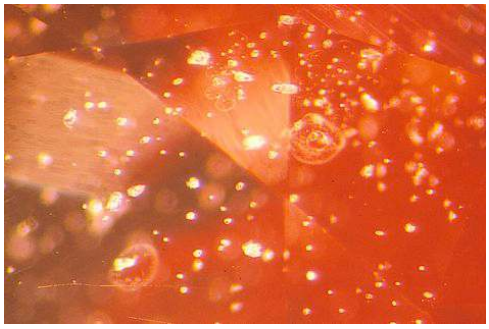




Baddeleyite in corundum at 1800°C



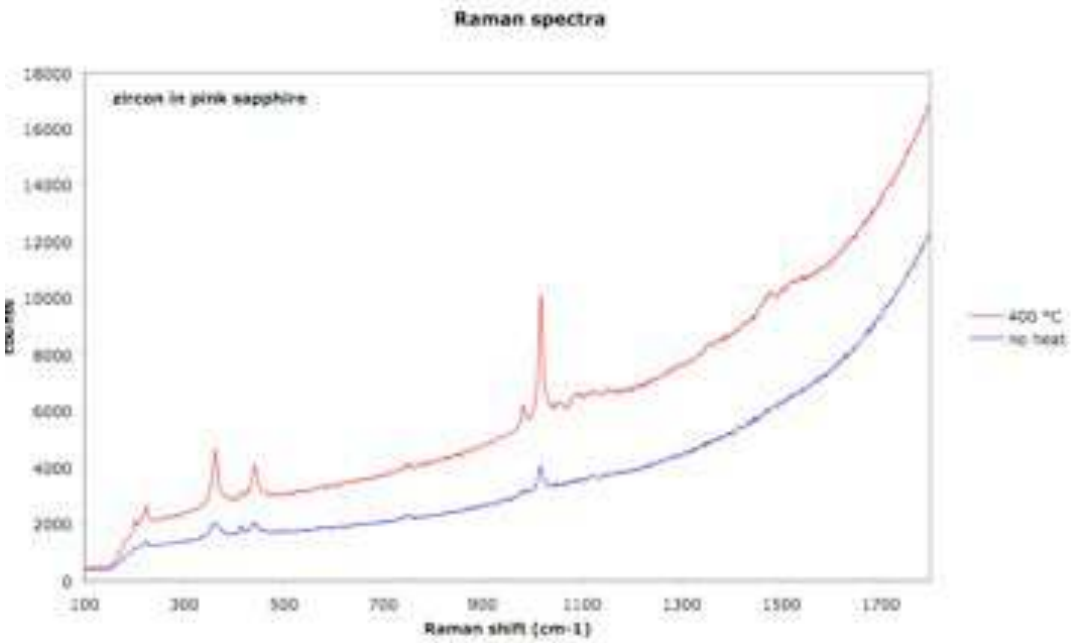




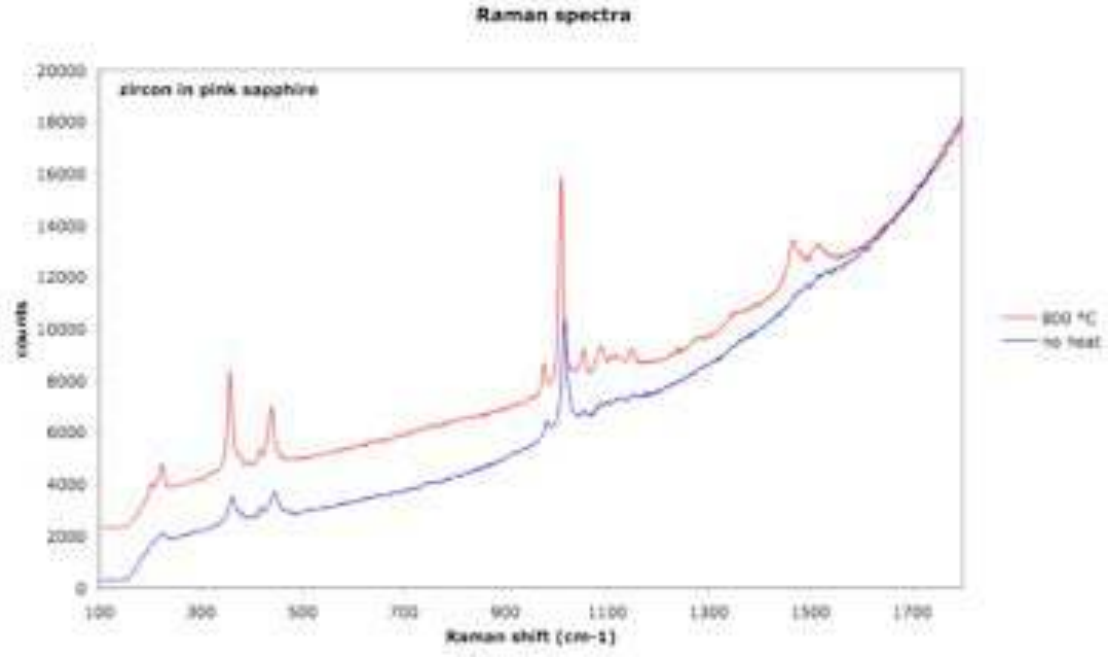
Chemical analysis (SEM EDS):
Baddeleyite ZrO_2 and silica glass and corundum

Baddeleyite forms whitish crusts
around altered zircons

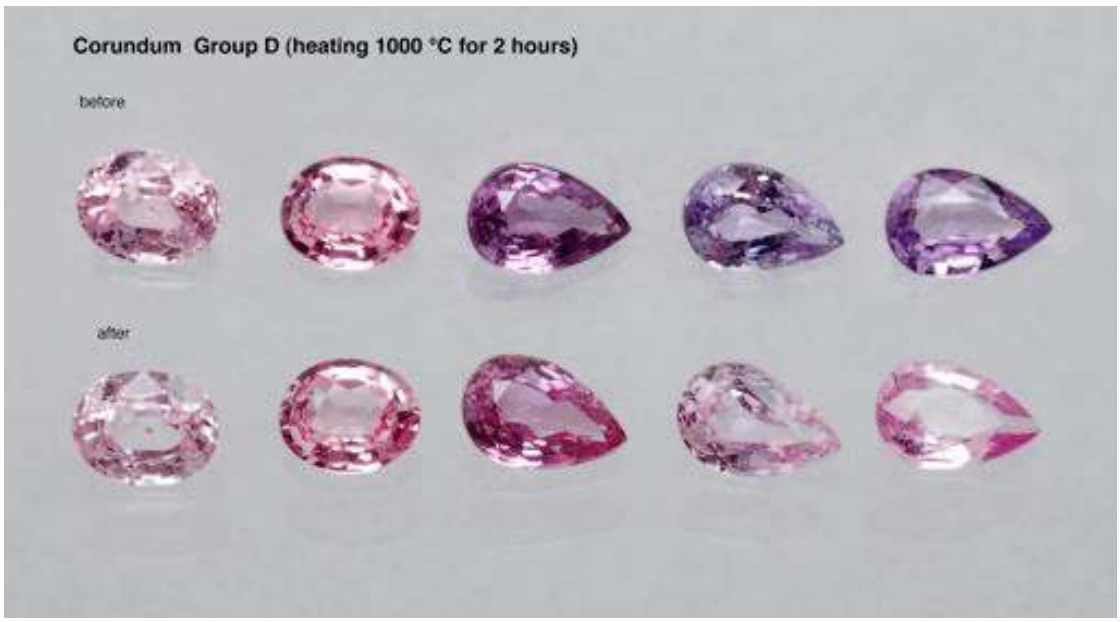
Zircon in corundum heated at 400°C



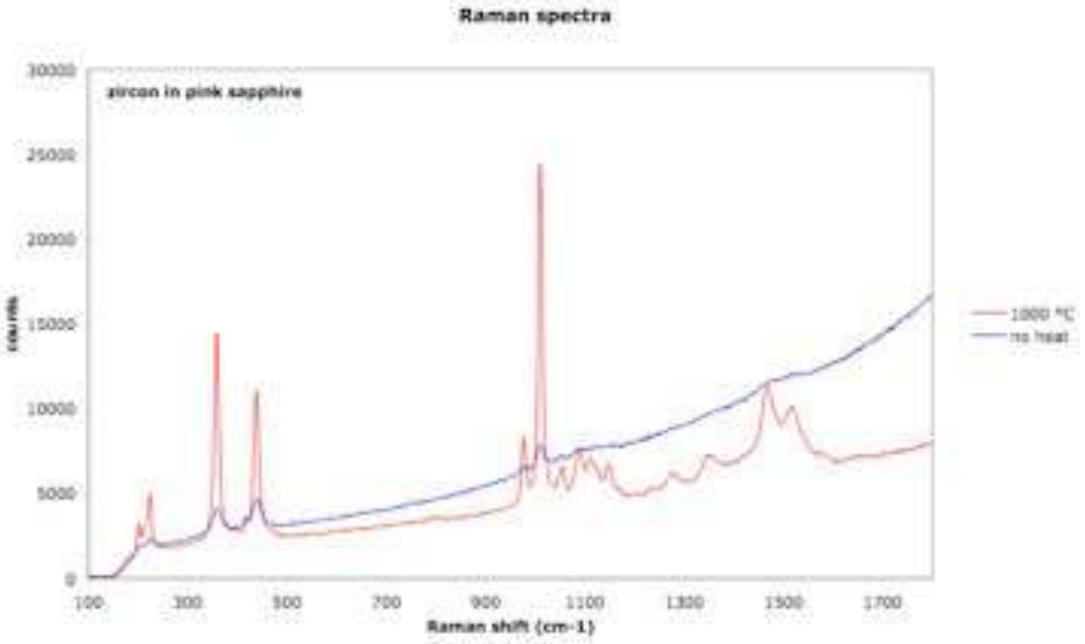
Zircon in corundum heated at 800°C



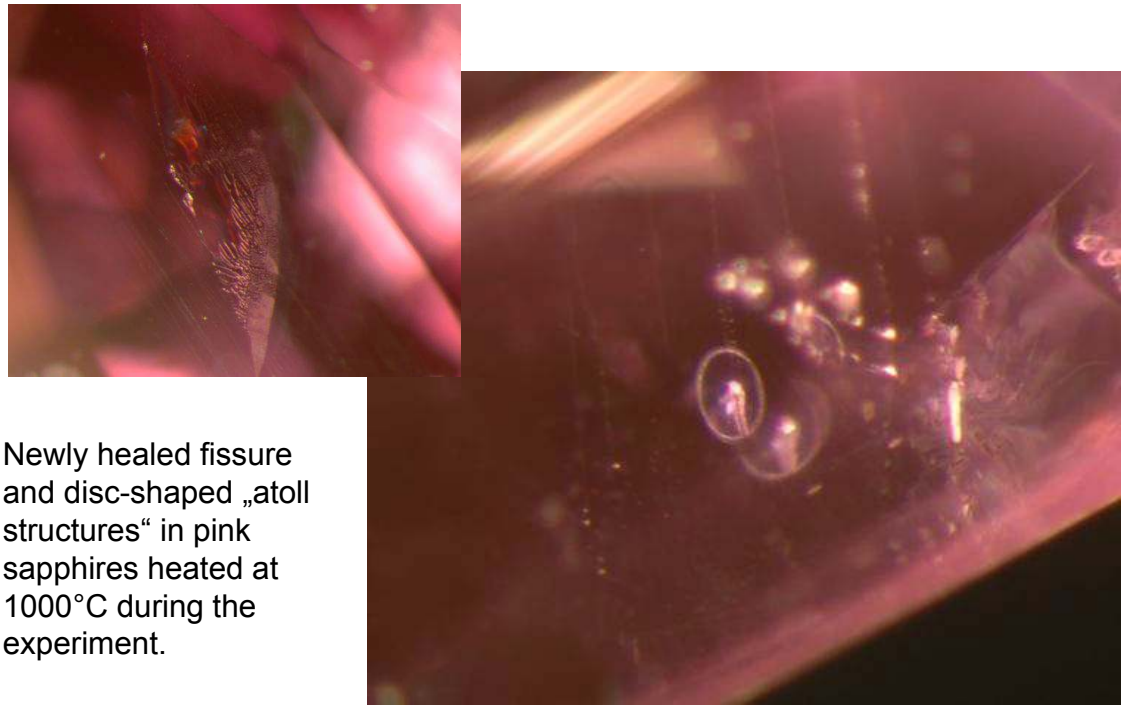
Zircon in corundum heated at 1000°C



Zircon in corundum heated at 1000°C

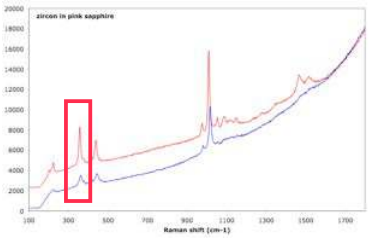


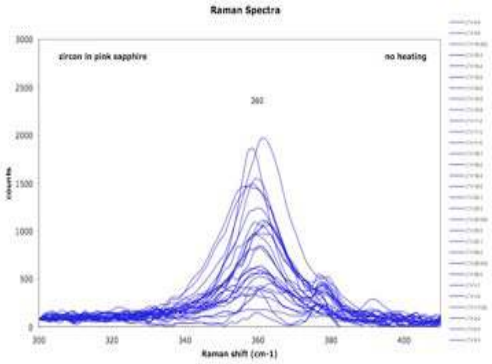
Zircon in corundum heated at 1000°C

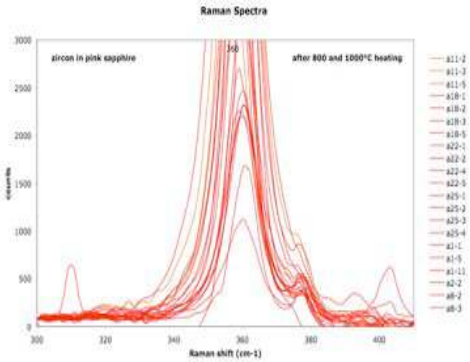


Newly healed fissure and disc-shaped „atoll structures“ in pink sapphires heated at 1000°C during the experiment.

Zircon: the Raman peak at 360 cm^{-1}



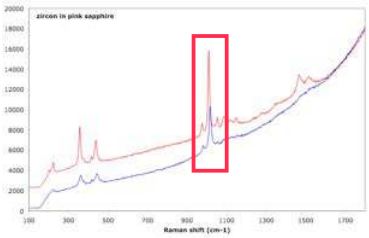


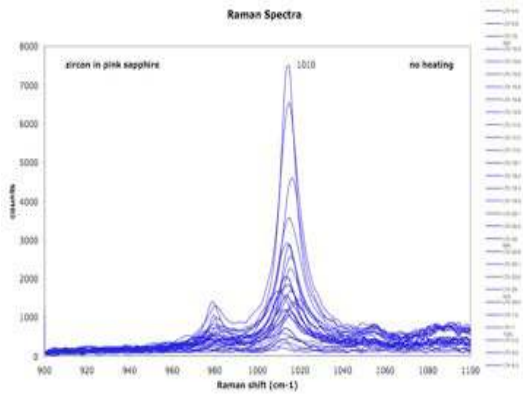


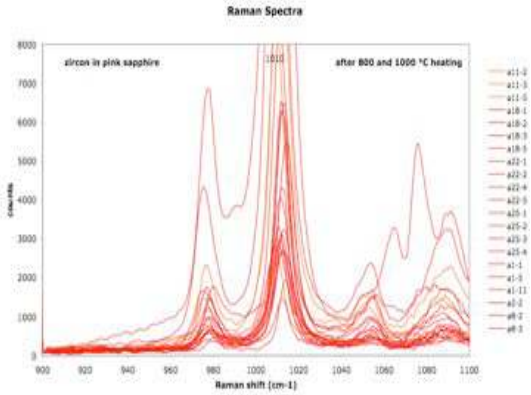
unheated

heated at 800 to 1000 °C

Zircon: the Raman peak at 1010 cm^{-1}



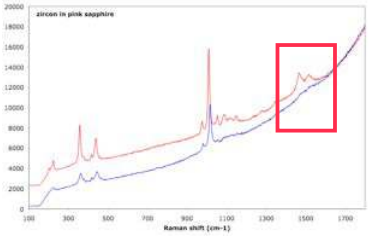


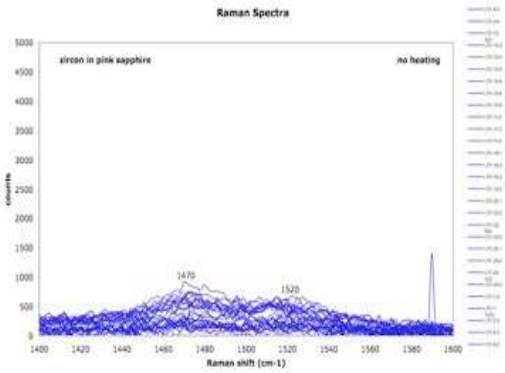


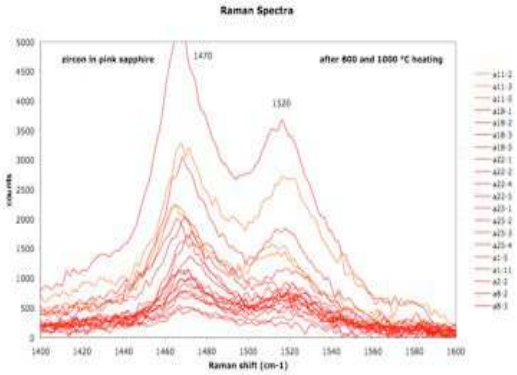
unheated

heated at 800 to 1000 °C

Zircon: the Raman peak at 1470 cm^{-1}



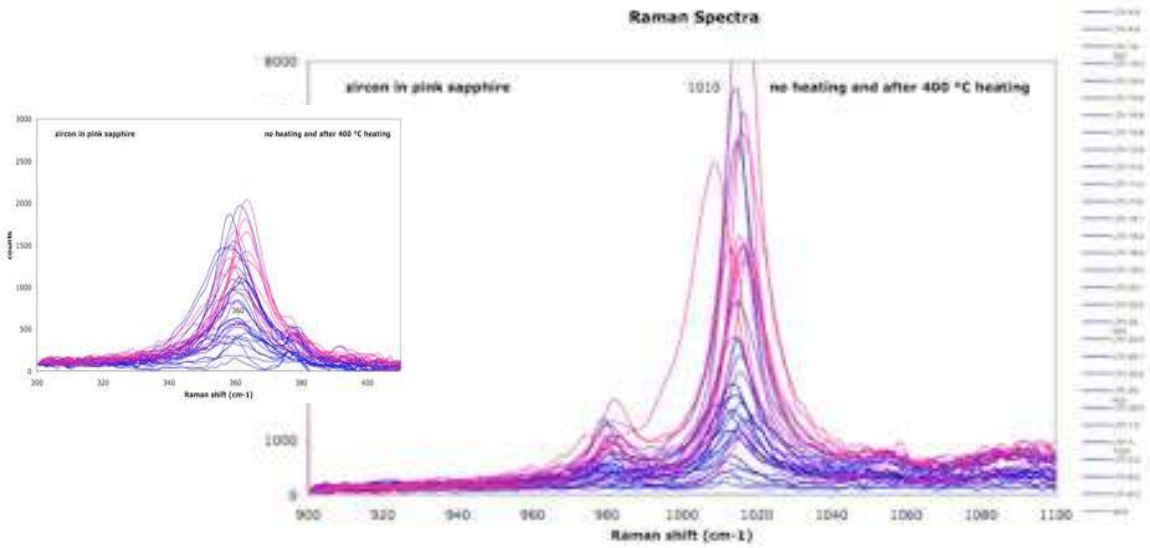




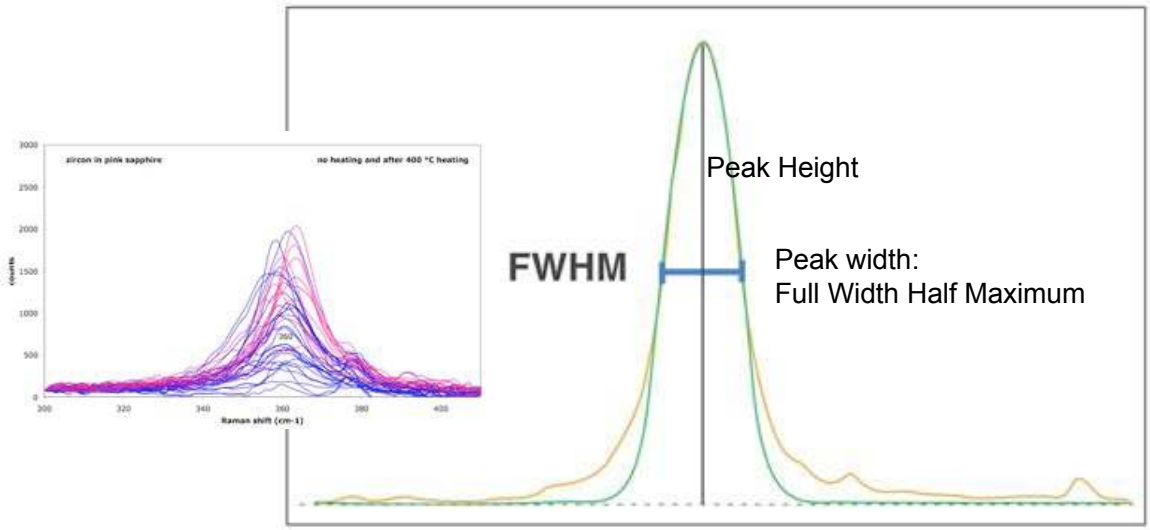
unheated

heated at 800 to 1000 °C

Zircon: Raman peaks at 400°C



The next step: measuring the peaks



The next step: measuring the peaks

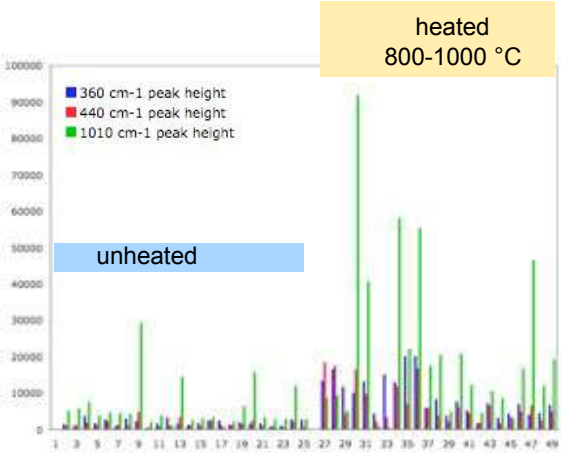
Difficulties:

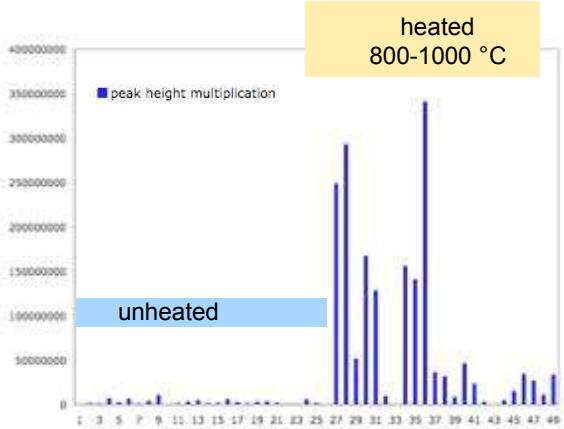
- The anisotropy of zircons has an influence on height and shape of Raman peaks
- The depth of zircon inclusions within a pink sapphire is reflected by various superposition effects
- Zircons at the surface may have changed by heat during cutting

Solution:

- measure not only one Raman peak,
  but the three most important peaks at 360,440, and 1010 cm^{-1}
- observe also photoluminescence peaks
- Analyse zircon inclusions always with the same analytical parameters
- Avoid zircon inclusions at the surface
- when ever possible analyse several zircon inclusions in a pink sapphire

The next step: measuring the peaks





Where do the stones come from...

Thank you for your attention