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

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

<table>
<thead>
<tr>
<th>Heating with diffusion</th>
<th>Heating with flux</th>
<th>Heating with high refractive glass flux, e.g., lead glass</th>
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<tr>
<td>Heating with glass flux, e.g., lead glass</td>
<td>Heating with borax flux, e.g., rubies from Mong Hsu (Burma)</td>
<td>effect: significant enhancement of transparency and colour and stability</td>
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<tr>
<td>Heating with chromium diffusion (shallow)</td>
<td>Heating with arc or high temperature heating, e.g., rubies from Indonesia</td>
<td>effect: creation of shallow colour zone</td>
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<tr>
<td>Heating with beryllium diffusion (lattice, bulk), e.g., corundum from Songea</td>
<td>Heating with high temperature heating, e.g., rubies from Myanmar</td>
<td>effect: significant colour modification</td>
</tr>
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</table>

Low temperature heating (<1000 °C), e.g., purplish sapphires become pink when heated in oxidising conditions.

Heating > 1000 °C, e.g., for geuda corundum, rubies from Thailand:

effect: colour modification; reducing visibility of inclusions.

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.

Difficult to detect with the microscope.
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!

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Microscopic features of heated corundum

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

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.

Perfect would be:

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

- An inclusion which changes in relation to the heating temperature

- An inclusion which is found very often in corundum

Zircon
Zircon in pink sapphire

Zircon is abundant!

Zircon inclusions change their appearance with increasing heating temperature!

unheated
approx. 1000 °C
approx. 1800 °C
Zircon

Zircon $\text{ZrSiO}_4$ 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

Increase in metamictisation

Experiment 1: Heating of zircon

Before heating

A: 400 °C
B: 600 °C
C: 800 °C
D: 1000 °C

After heating
Heating of zircon

Increase in temperature

1000 °C
800 °C
600 °C
400 °C
unheated

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Heating of zircon

Zircon References: Group B (600 °C heating for 2 hours)

Zircon References: Group C (800 °C heating for 2 hours)
Heating of 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

Baddeleyite ZrO₂ precipitation (dendritic) on the surface of beryllium diffusion treated corundum
**Baddeleyite in corundum at 1800°C**

Chemical analysis (SEM EDS): Baddeleyite $\text{ZrO}_2$ and silica glass and corundum

Baddeleyite forms whitish crusts around altered zircons

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**Zircon in corundum heated at 400°C**

![Raman spectra](image)

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Zircon in corundum heated at 800°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\(^{-1}\)

![Raman Spectra](image1)

unheated

heated at 800 to 1000 °C

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

![Raman Spectra](image2)

unheated

heated at 800 to 1000 °C

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

unheated

heated at 800 to 1000 °C

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Zircon: Raman peaks at 400°C

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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...
... Madagascar

Thank you for your attention