A Gemmological Approach to Distinguishing Natural from Synthetic Rubies: LA-ICP-TOF mass spectrometry provides new insights

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**Price Comparison: Natural vs Synthetic Rubies**

### Natural Rubies

Natural rubies > $3000 per carat

Good quality natural rubies ≈ $10,000 to $18,000 per carat

In 2012, a 6.04 ct Burmese ruby sold for $551,000 USD per carat

In 2014, the 8.62 ct Burmese Graff Ruby sold for $8.6 Million = $997,679 per carat*

### Synthetic Rubies

Verneuil = $1 to $5 per carat

Hydrothermal ≈ $90 per carat

Knirschka ≈ $90 per carat

Chatham ≈ $24 to $400 per carat

Kashan ≈ $150 - $500 per carat

Ramaura = $150 to $750 per carat

In the trade, prices would be considerably lower

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*https://www.graff.com/collections/high-jewellery/the-graff-ruby/*
Differences between Natural, Synthetic, and Treated Natural or Synthetic Rubies

- Identifying the subtle differences can be difficult because of:
  - Overlapping physical properties and some trace elements
  - Presence of similar inclusions or growth features
  - Absence of inclusions or growth features
  - In addition, the setting of a gemstone may also interfere with analysing trace elements and observing internal features
Analytical Techniques

Optical Microscopy
-examine inclusions and growth features

Raman Spectroscopy
-identify inclusions
INCLUSIONS IN NATURAL RUBIES

POSSIBLY CONFUSING INCLUSIONS IN NATURAL RUBIES vs SYNTHETIC RUBIES

Rutile needles

Apatite

Photos © H.A. Hänni

Crystal Pulling Synthetic (Czochralski)

Carbonates

Flame Fusion Synthetic (Verneuil)

Photos © H.A. Hänni, SSEF
GROWTH PATTERNS IN
NATURAL RUBIES VS SYNTHETIC RUBIES

Characteristic growth structures in rubies from Mong Hsu

Zoning in a Ramuara Synthetic

Colour swirls in a natural ruby

Chevron growth pattern in a hydrothermal beryl

Hydr. Ruby

Hydr. Emerald

Photos © H.A. Hänni, SSEF
Natural Ruby Heated with Flux

Cracked Synthetic Verneuil Ruby Heated with Flux

Knischka Synthetic Ruby with Flux Residue

Platinum flakes
IRON STAINING VS FLUX RESIDUE

Iron Staining in Natural Ruby

Orange Flux in Synthetic Ruby (Ramaura)
# Possible Sources of Trace elements in Synthetic Rubies

<table>
<thead>
<tr>
<th>Melt</th>
<th>Feed</th>
<th>Apparatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Czochralski Flame Fusion</td>
<td>Alumina and Cr$_2$O$_3$</td>
<td>Iridium Crucible</td>
</tr>
<tr>
<td></td>
<td>Alumina and Cr$_2$O$_3$</td>
<td></td>
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<tr>
<td><strong>Flux</strong></td>
<td><strong>Feed</strong></td>
<td></td>
</tr>
<tr>
<td>Chatham</td>
<td>Li$_2$O-MoO$_3$-PbF$_2$ and -or PbO</td>
<td>Pt Crucible</td>
</tr>
<tr>
<td>Kashan</td>
<td>Na$_3$AlF$_6$</td>
<td>Pt Crucible</td>
</tr>
<tr>
<td>Knischka</td>
<td>Li$_2$O-WO$_3$-PbF$_2$, PbO, Na$_2$W$_2$O$_7$, and Ta$_2$O$_5$</td>
<td>Pt Crucible</td>
</tr>
<tr>
<td>Douros</td>
<td>PbF$_2$ or PbO$_4$</td>
<td>Pt Crucible</td>
</tr>
<tr>
<td>Ramaura</td>
<td>Bi$_2$O$_3$-PbF$_2$, also REE dopant added to the flux La$_2$O$_3$</td>
<td>Pt Crucible</td>
</tr>
<tr>
<td><strong>Hydrothermal</strong></td>
<td>Alumina or aluminum hydrates partially dissolved in an aqueous medium with Cr compounds such as Na$_2$Cr$_2$O$_7$</td>
<td>Metal autoclave containing Fe, Ni, and Cu</td>
</tr>
</tbody>
</table>

Reference: Muhlmeister et al. 1998 and sources within
Analytical Techniques

ED-XRF Spectroscopy

LA-ICP-TOF-MS

Major and Trace elements

LA-ICP-MS detected:
- Pt
- elevated La, Bi, Pb
The graphs illustrate the relationship between Rh [ppm] and Pt [ppm] on the left, and Rh [ppm] and W [ppm] on the right. The data points are color-coded and labeled according to the following categories:

- **Natural**
- **Synthetic, Crystal Pulling, Czochralski**
- **Synthetic, Hydrothermal**
- **Synthetic, Flame Fusion, Verneuil**
- **Synthetic, Flame Fusion, Induced Fingerprint**

Each category is represented by a specific symbol and color to differentiate between them.
## Synthetic

<table>
<thead>
<tr>
<th>Method</th>
<th>Typically very pure</th>
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</thead>
<tbody>
<tr>
<td>Flame Fusion, Verneuil</td>
<td>Typically very pure</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>Typically very pure</td>
</tr>
<tr>
<td>Crystal Pulling, Czochralski</td>
<td>Typically very pure</td>
</tr>
</tbody>
</table>

## Synthetic Flux
(values in ppm)

<table>
<thead>
<tr>
<th>Location</th>
<th>Na</th>
<th>Ni</th>
<th>V</th>
<th>Kashan</th>
<th>Pt</th>
<th>W</th>
<th>Pt</th>
<th>Mo</th>
<th>Ga</th>
<th>Chatham</th>
<th>Pt</th>
<th>W</th>
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<th>Mo</th>
<th>Ga</th>
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<td>bd – 1371.13</td>
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<td>0.07</td>
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<td>Ramaura</td>
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### Note
- **bd**: Below detection limit.
SUMMARY AND CONCLUSIONS

- Natural rubies typically have many natural mineral inclusions.
- It is important to always combine meticulous optical microscopic observations with elemental analyses.
- In the presence of similar inclusions or the absence of any inclusions, LA-ICP-TOF-MS results may help differentiate natural from synthetic rubies.
- Elevated levels of Pt, Rh, W, Ni, Mo, Na, La, Pb, and Bi can indicate a synthetic flux ruby.
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