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
Knischka ≈ $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

* 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

- Rutile needles
- Carbonates

POSSIBLY CONFUSING INCLUSIONS IN NATURAL RUBIES vs SYNTHETIC RUBIES

- Apatite
- Crystal Pulling Synthetic (Czochralski)
- Flame Fusion Synthetic (Verneuil)

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GROWTH PATTERNS IN NATURAL RUBIES VS SYNTHETIC RUBIES

Characteristic growth structures in rubies from Mong Hsu

Zoning in a Ramuara Synthetic

Chevron growth pattern in a hydrothermal beryl

Colour swirls in a natural ruby

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</td>
<td>Alumina and Cr$_2$O$_3$</td>
<td>Iridium Crucible</td>
</tr>
<tr>
<td>Flame Fusion</td>
<td>Alumina and Cr$_2$O$_3$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flux</th>
<th>Flux</th>
<th></th>
</tr>
</thead>
<tbody>
<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>
</tbody>
</table>

| Douros        | PbF$_2$ or PbO$_4$   | Pt Crucible      |
| Ramaura       | Bi$_2$O$_3$·PbF$_2$, also REE dopant added to the flux La$_2$O$_3$ | Pt Crucible      |

| Hydrothermal  | Alumina or aluminum hydrates partially dissolved in an aqueous medium with Cr compounds such as Na$_2$Cr$_2$O$_7$ | Metal autoclave containing Fe, Ni, and Cu |

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

ED-XRF Spectroscopy

Major and Trace elements

LA-ICP-TOF-MS

LA-ICP-MS detected:
- Pt
- elevated La, Bi, Pb
### Synthetic

**Flame Fusion, Verneuil**
- Typically very pure

**Hydrothermal**
- Typically very pure

**Crystal Pulling, Czochralski**
- Typically very pure

### Synthetic Flux (values in ppm)

<table>
<thead>
<tr>
<th>Kashan</th>
<th>Knischka</th>
<th>Chatham</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>Ni</td>
<td>W</td>
<td>Mo</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>Ga</td>
</tr>
<tr>
<td>bd - 1371.13</td>
<td>0.35 - 4.49</td>
<td>bd - 13.68</td>
</tr>
<tr>
<td>bd - 197.04</td>
<td>0.07 - 146.58</td>
<td>bd - 267.45</td>
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<tr>
<td>4.82 - 42.68</td>
<td></td>
<td>0.08 - 16.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Douros</th>
<th>Ramaura</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>Rh</td>
<td>La</td>
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<tr>
<td>Ga</td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
</tr>
<tr>
<td>0.13 - 15.91</td>
<td>6.57 - 262.95</td>
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<tr>
<td>bd - 39.70</td>
<td>bd - 365.75</td>
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<tr>
<td>244.80 - 380.61</td>
<td>bd - 2231.79</td>
</tr>
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<td></td>
<td>bd</td>
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<tr>
<td></td>
<td>bd</td>
</tr>
<tr>
<td></td>
<td>30.45 - 551.85</td>
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</tbody>
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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
Special Thanks

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Thank you for your attention