

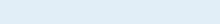
SGG Zentralkurs | June 2023 NEWS FROM SSEF with a focus on East Africa

Presentation by PD Dr. Michael S. Krzemnicki

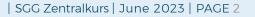


Contents

- Corundum: Colour centres, Irradiation treatment and
 low-Temperature treatment
- Paraiba tourmaline
- Spinel
- Garnet
- Chrysoberyl & Alexandrite
- News



Corundum varieties





Colour Centres in Corundum: Tenebrescence



Unstable Colouration of Padparadscha-like Sapphires

Michael S, Krzemnicki, Alexander Klumb and Judith Braun

ABSTRACT: After the October 2016 discovery of a new gem deposit at Bemainty near Ambatondrazaka, Madagascar, a number of sapphires with padparadschalike colour entered the trade. However, most of these stones were found to have unstable colour, which changes from pinkish orange to more-or-less pure pink after a few weeks in daylight. In this study, the authors investigate the colour stability of padparadscha-type sapphires of metamorphic origin—mainly those originating from Madagascar (Ambatondrazaka and Ilakaka) and Si Lanka. The 48 samples could be separated into three groups after colour-stability testing: sapphires that did not show a noticeably different appearance (case A); sapphires with a slight-to-moderate colour difference within the padparadscha range (case B); and fancy-colour sapphires showing a distinct change in appearance that fell outside of the padparadscha range (case C). The last situation was especially common for the stones from Ambatondrazaka, thus revealing that careful colour-stability testing is mandatory for proper gemmological identification of any sapphire showing a yellow to orange colour component.

The Journal of Gemmology, 36(4), 2018, pp. 346–354, http://doi.org/10.15506/JoG.2018.36.4.346 © 2018 The Gemmological Association of Great Britain

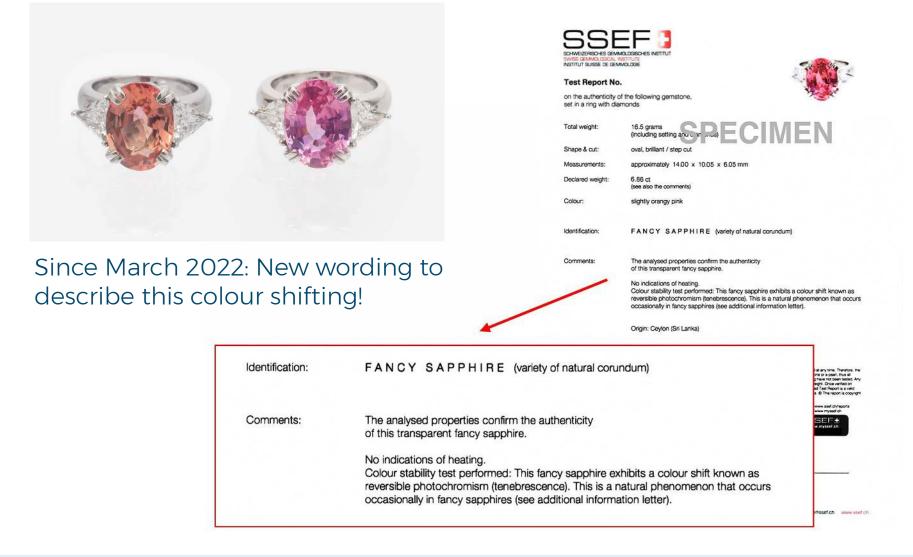
346 THE JOURNAL OF GEMMOLOGY, 36(4), 2018

Colour centres in corundum, specifically important for yellow, orange and padparadscha-like colours.

Not all of these colour centres are stable. Thus the colour may shift over time, but also be activated by exposing the stone to an appropriate radiation.



Colour Centres in Corundum: Reversible Photochromism (Tenebrescence)





Irradiation Treatment of Corundum



Photos and Experiment: © T. Leelawatanasuk, GIT Thailand

Since about two years, we have reliable information that rubies of purplish red tint (e.g. from Mozambique) and purplish-pink sapphires (e.g. from Madagascar) are treated by a small number of individuals using cancer radiotherapy equipment.

This irradiation treatment may induce and/or activate colour centres in corundum that result in a shift to a more attractive red or pink hue.

Usually, the colour is not fully stable, thus shifting back at least partially or fully after irradiation.



Irradiation Treatment of Corundum

Since many years, the SSEF tests the colour stability of yellow, orange and padparadscha coloured corundum.



New additional test at SSEF for the colour stability of rubies

Date : 01/03/2022 Category : Research

In light of information gathered over the past few months, we have now added rubies to this colour stability testing protocol, specifically but not limited to rubies originating from Mozambique....

READ MORE

see: <u>www.ssef.ch/news</u>

In March 2022, we informed our clients about this new treatment and that we expanded the colour stability testing to certain rubies.

To better understand this treatment and to find criteria for detection, we started a research project including irradiation experiments using a linear accelerator in Switzerland.



THIS IS NEXT.

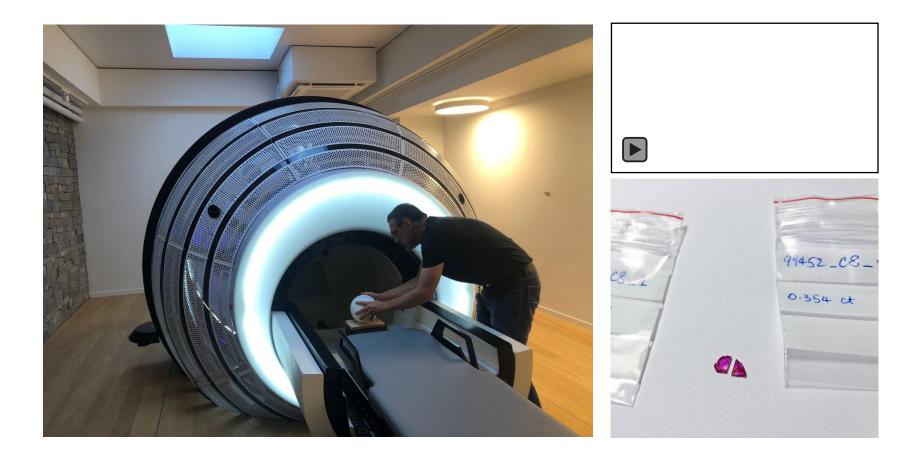
ZAP-X° GYROSCOPIC RADIOSURGERY





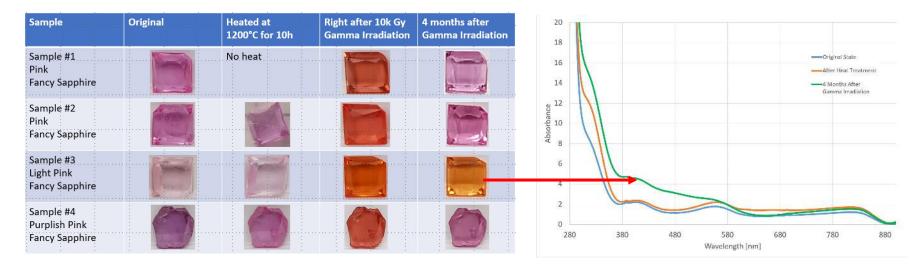
Irradiation Experiments with Gemstones

We collaborate for this with a specialised Swiss institution (SNRC).





Irradiation Experiments with Gemstones



Distinct colour change after irradiation in pink to purple sapphires, most were not stable.

But no colour shift in all our Mozambique rubies of saturated red colour after irradiation (in accordance with findings of other labs).





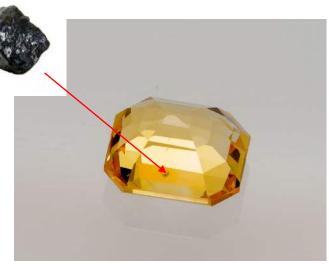
Irradiation Treatment: Current Status of Research

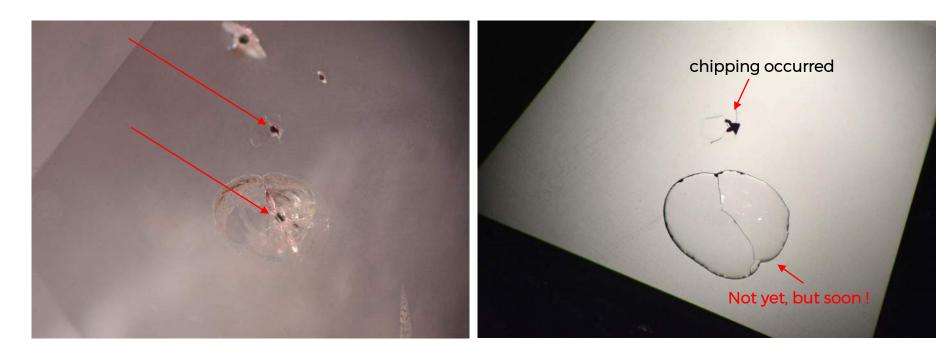
- Irradiation treatment of corundum is known since many decades.
- So far, no scientific method to positively detect this treatment. Several gem labs (incl. LMHC) do research on this topic.
- To avoid colour shifting issues, most gem labs expand colour stability testing to include rubies, specifically if they show an orangey-red hue.
- SSEF colour stability testing on many hundred Mozambique rubies: We never observed a ruby with colour instability.
- Although not a proof, that such a ruby was not irradiated, it confirms at least that its colour is stable !
- All saturated red rubies irradiated by SSEF and other labs did not show any noticeable colour shift. We assume that this irradiation treatment is mostly successful for purplish red to purplish pink corundum of medium to low saturation.



Natural Irradiation Damage

Thorianite (ThO_2) or other radioactive inclusion near the surface may result in a (small) chipping damage as a consequence of the decay of U to Pb over (geological) time periods.







Low-Temperature heating of Corundum



Heating of corundum:

- Traditionally at about 1200-1400 °C to enhance colour significantly. Inclusions (e.g. rutile needles, zircon) are mostly transformed.
- At higher temperatures (>1500 °C) commonly for diffusion treatment or artificially healing of fissures using a (borax) flux.
- At about 700 1000 °C (referred to as low-T heating in the trade). Inclusions may remain intact and usually only minor colour enhancement of the stone.



Classic Detection



Characteristic atoll-structure

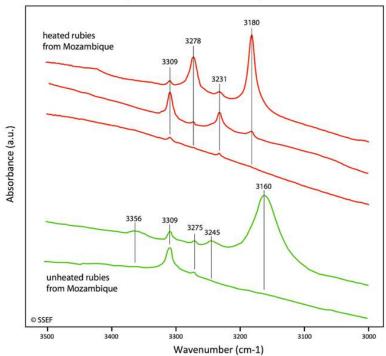
50x magnification, easy to see

Characteristic atoll-structure 70x magnification, difficult to see

Such evident features for heating are rarely seen in corundum heated at low temperatures.



FTIR spectroscopy



FTIR-Spectra of Mozambique Rubies



PRESS RELEASE

FOR IMMEDIATE RELEASE CONTACT: Dr. Michael S. Krzemnicki FGA gemlab@ssef.ch

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 Sept 2018 See <u>https://www.ssef.ch/press-releases/</u>

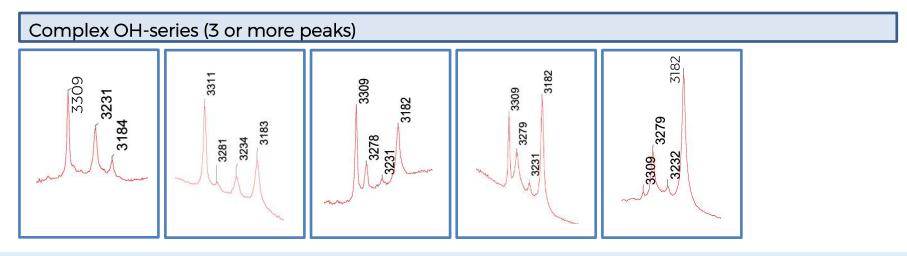


FTIR spectroscopy

Heated Mozambique Rubies:

Samples from Gemfields (heated by Gemfields) and the Bangkok trade.



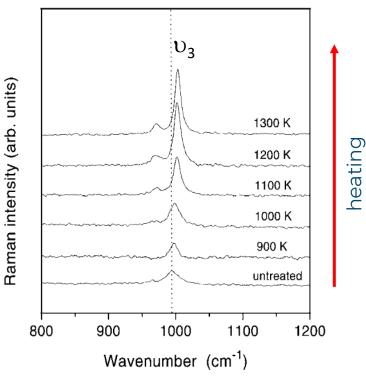




Zircon inclusions may provide important information about heat treatment (and origin) of corundum.



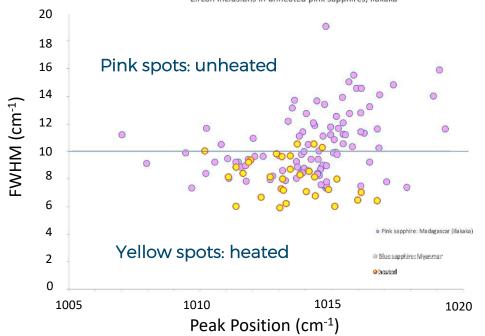
"Hot" pink sapphire from Ilakaka (Madagascar) and small zircon inclusions in such a pink sapphire.



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





Large overlap of unheated and heated pink sapphires from **Ilakaka (Madagascar)**.



cautiously to avoid misinterpretations.

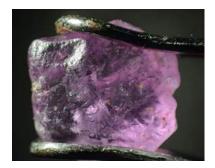
SGG Zentralkurs | June 2023 | PAGE 17

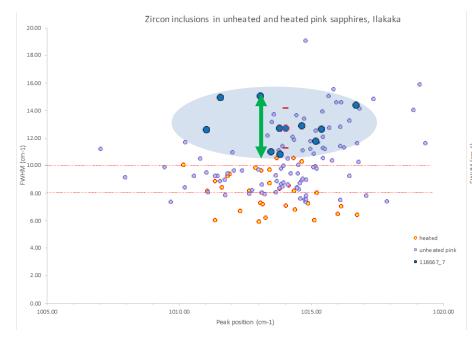
Zircon inclusions in unheated pink sapphires, Ilakaka

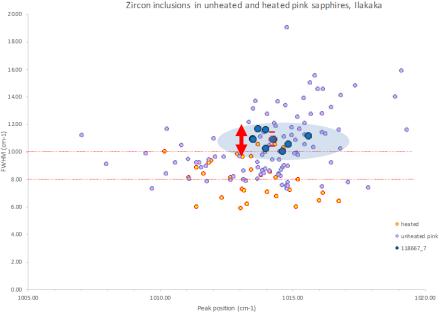
 υ_3 versus FWHM(υ_3) scatterplot

SSEF

Heating experiment (1000 °C) of pink sapphire, Madagascar with numerous zircon inclusions.







FWHM of zircons before

FWHM of zircons after heating

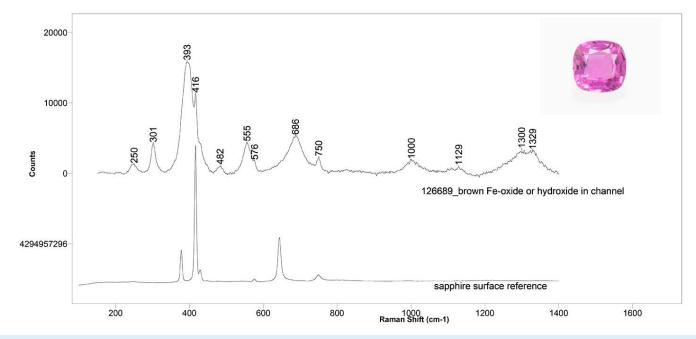


Goethite (Fe-hydroxide), diaspore (Al-hydroxide), and other inclusion minerals as important markers for unheated corundum!

Figure 2. Left: This Sri Lankan supplite bosts a blocky iron sulfide inclusion blocky iron sulfide inclusion with a surface-reaching coacted with yellow limonite. Right: After heating in air to 380°C, the limonite coating on both the sulfide and the related fracture changed to tomiscrographs by 11. Koivinla, magnified 10x.

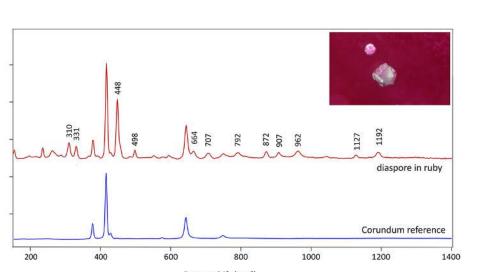


from Koivula 2013





Goethite (Fe-hydroxide), diaspore (Al-hydroxide), and other inclusion minerals as important markers for unheated corundum!



Raman shift (cm⁻¹)

1 2023 SSEF Newsletter March 2023 issu https://www.ssef.ch/ssef-news/



New and additional criteria to detect low-T heated pink sapphires applied by SSEF

Heat treatment of ruby, sapphire and other colour varieties of corundum is one of the main issues for the gem trade. As such, detecting such treatment is a major task of gemmological laboratories

37TH IGC CONFERENCE



IGC 2023: 23 -27 OCTOBER IN TOKYO, JAPAN

PHASE TRANSFORMATIONS AS IMPORTANT MARKERS FOR HEAT TREATMENT DETECTION IN CORUNDUM AND OTHER GEMSTONES

Michael S. Krzennicki^{1,2}, Piene Lefevre¹, Wei Zhou¹

¹Swiss Gemmological Institute SSEF, Acschengtaben 26, CH 4051 Basel, Switzerland ²Department of Environmental Sciences, Bernoullistrasse 36, University Basel, Switzerland

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Keywords: Heat treatment, disspore, grothite, dehydration, Raman spectroscopy

Introduction

Detection of heat treatment of unity and suppliire and other colour varieties of corundum is a major issue for the trade and laboratories alike. Heat treatment of corundum is commonly applied in a large temperature range from about 700 to 1200 °C in both, exidizing and reducing conditions

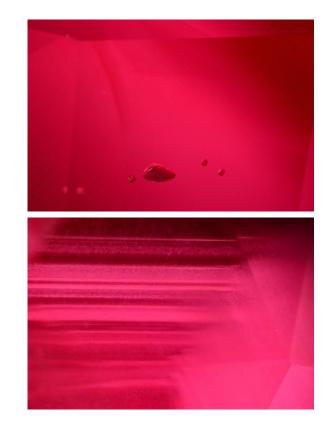
Traditionally, the detection of corundum heat treatment is based mainty on meticulous microscopic observation, da to concerne of the heating process, internal features (e.g. fluid and solid inclusion-zoning features) may be affected and altered (Gibbelin & Kovala 2006) and by this prostraightforward evidence of heat treatment. In general, characteristic heating features (e tension cardes no und inclusions, see Figure 1) become more prominently visible with it temperature (and heating duration). Far more challed first in the microscopic detection of no called flow desperature' lacted coundant. In these stones which are lacted at about 700 °C to 1100 °C t only very minute or even no alterations of inclusions may be observed under the microscope (Hughes et al. 2022). Another classic approach is to check for "chalky" fluorescence reactions un shortwave ultraviolet light. However, such reactions can generally only be expected at higher heating temperatures well beyond 1100 °C.

Heat treatment detection is also very much relying on FTIR and Raman spectroscopy. In FTIR, the focus is very much on the presence and intensity of OH related absorption peaks. Namely the 3309, 3232 and 3185 cm⁻¹ series in metamorphic corvindum is considered a strong indication for artificial heat treatment (Smith 1995; Beam & Rossman 2006; Saesenw et al. 2020; Pardieu et al. 2015; Krzemnicki 2019). The presence or absence of a Mg-O related band at 3160 cm⁻¹ is another important

Counts

Estrela de Fura 55.22 ct, Mozambique





USD 34.8 million at Sotheby's Auction, 8th of June, in New York.

New World Record for a ruby and any coloured gemstone at auction so far.



Paraiba Tourmaline





Paraiba Tourmaline



Paraiba tourmaline (Brazil) of 14.20 ct with indications of heating. Sold for ca. US\$ 805,000 at Christie's Hong Kong in May 2021.



Paraiba tourmaline and diamond ring. The tourmaline weighs 21.63 ct, is of Mozambique origin and it is currently not possible to determine if the tourmaline has been heated or not. Sold for ca. US\$ 532,000 by Sotheby's Geneva in May 2022.



10.13 ct copper- and manganesebearing tourmaline from Nigeria, also called 'Paraiba tourmaline' in the trade. It is currently not possible to determine if the tourmaline has been heated or not. Sold for US\$ 239,400 at Sotheby's New York in December 2022. Photo: Sotheby's.

Nigeria: Edeko

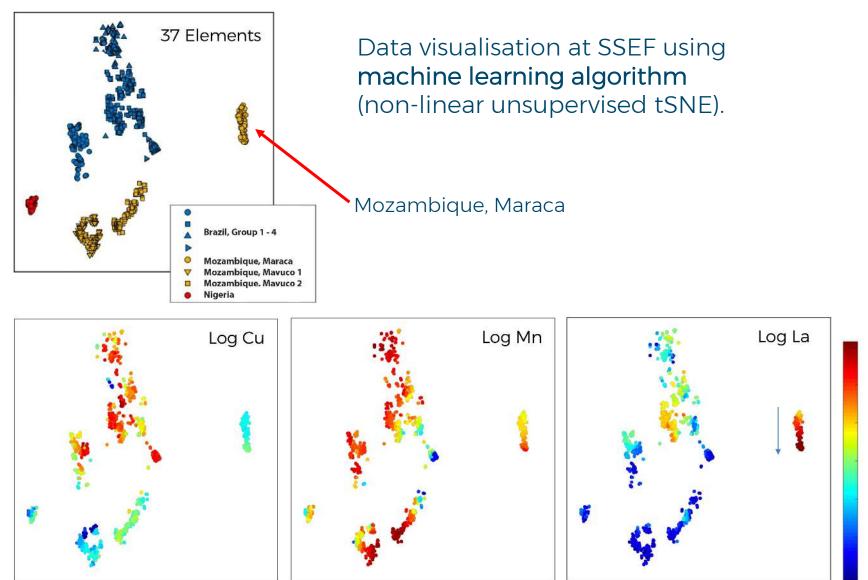
Brazil: Paraiba & Rio Grande do Norte Mozambique: Mavuco & Maraca

Map © Wikicommons



| SGG Zentralkurs | June 2023 | PAGE 23

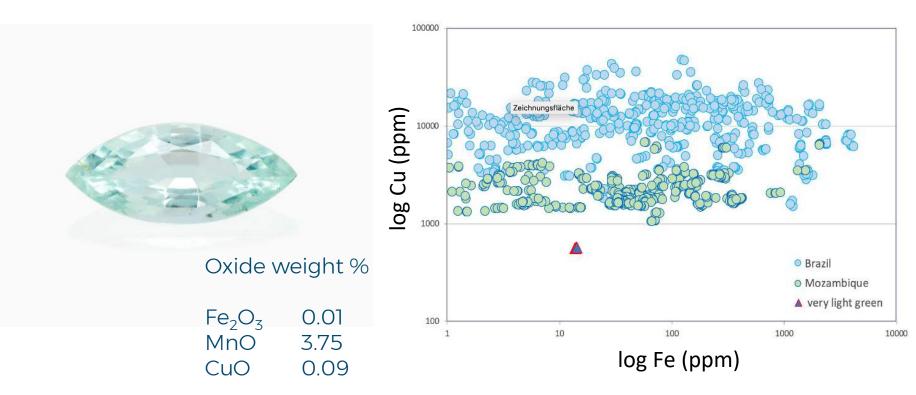
Machine Learning for Paraiba Origin Determination





Paraiba tourmaline or not?

Mozambique tourmaline containing low amount of copper.



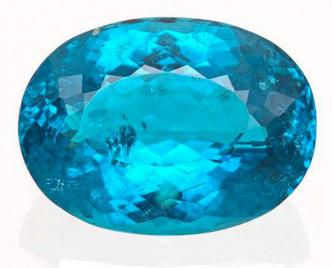
Not considered Paraiba tourmaline!

See also updated LMHC information sheet No. 6: https://www.lmhc-gemmology.org/gemstones



Quiz: Paraiba tourmaline or not?

Pair of tourmalines from same client tested recently at SSEF.



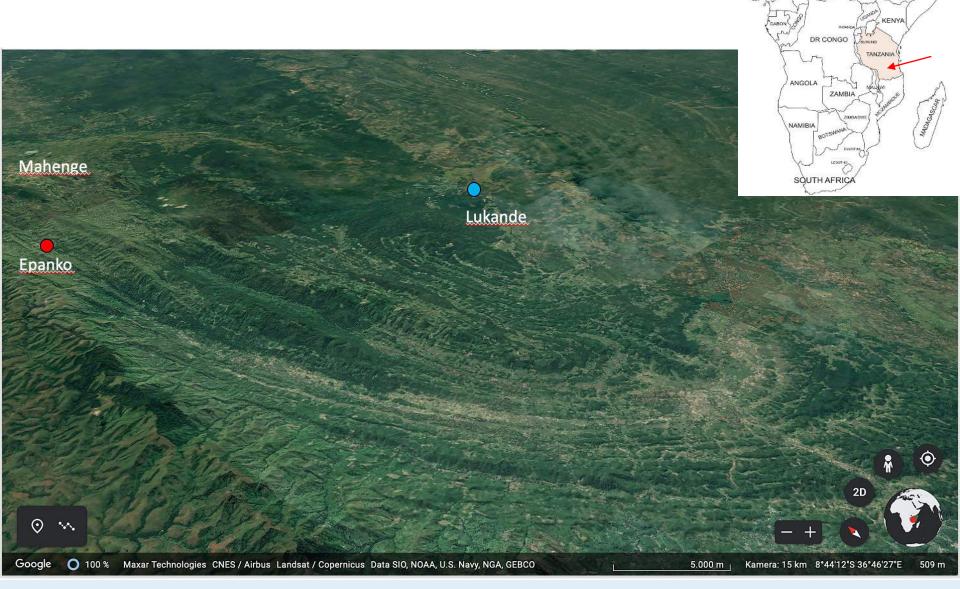


Oxide weight %

Fe₂O₃ 0.01 MnO 0.98 CuO 0.24 Fe₂O₃ 2.00 MnO 0.99 CuO b.d.



Spinels from Lukande and Epangko, near Mahenge, Tanzania





Co-bearing Spinel from Lukande, south of Mahenge, Tanzania

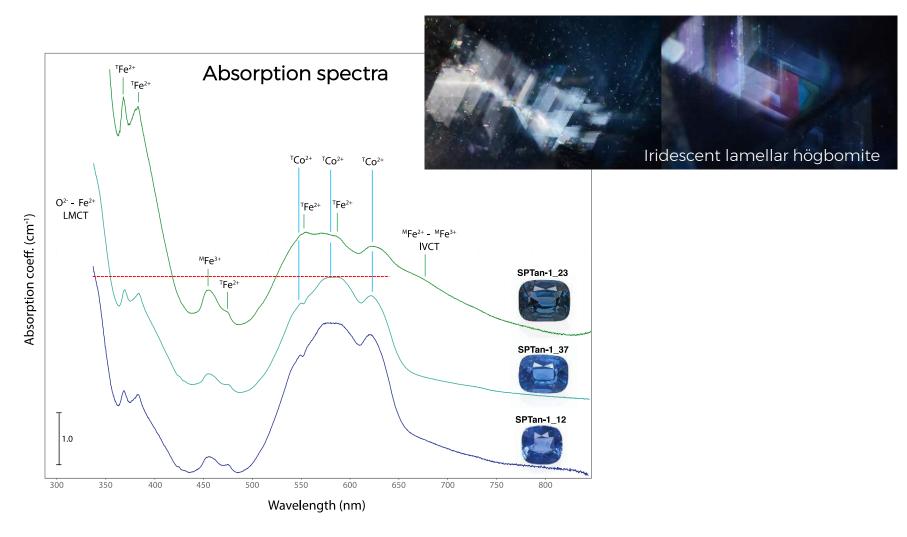


Photo: SSEF



Co-bearing Spinel from Lukande, south of Mahenge, Tanzania

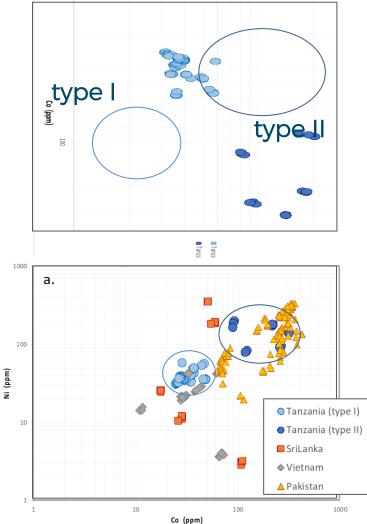
Not all blue spinel from this new source is Co-spinel !





Co-bearing Spinel from Lukande, south of Mahenge, Tanzania

Trace element comparison of Co-spinel type I vs type II from Lukande



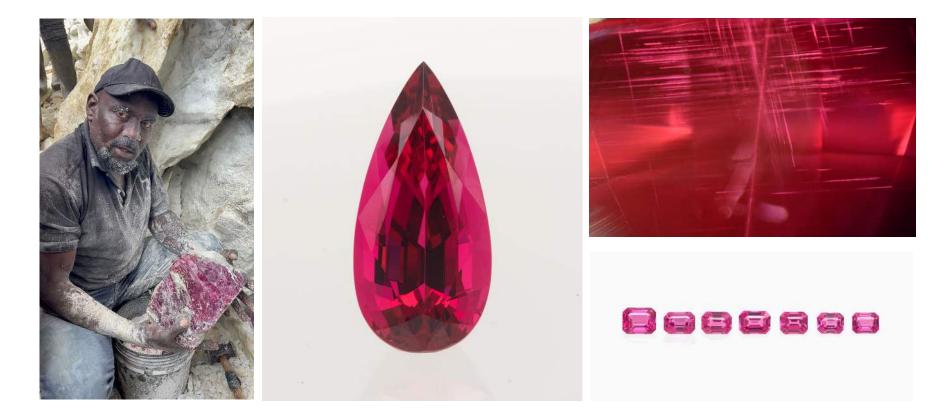


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| SGG Zentralkurs | June 2023 | PAGE 30

New Spinel from Epangko near Mahenge, Tanzania

New production of pinkish red spinel from the "classical" deposit in Epangko, near Mahenge (Morogoro region, Tanzania.





near Mahenge, Tanzania

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angko spinel deposit, ar Mahenge, Tanzania





Ant Hill Garnet (Pyrope)

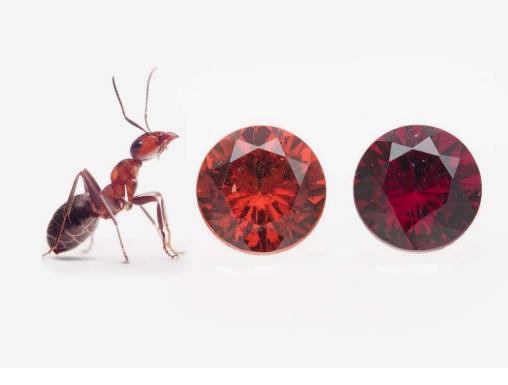


Photo © Mindat.c NAVAJO NATION Utah Colorado New Arizona Mexico

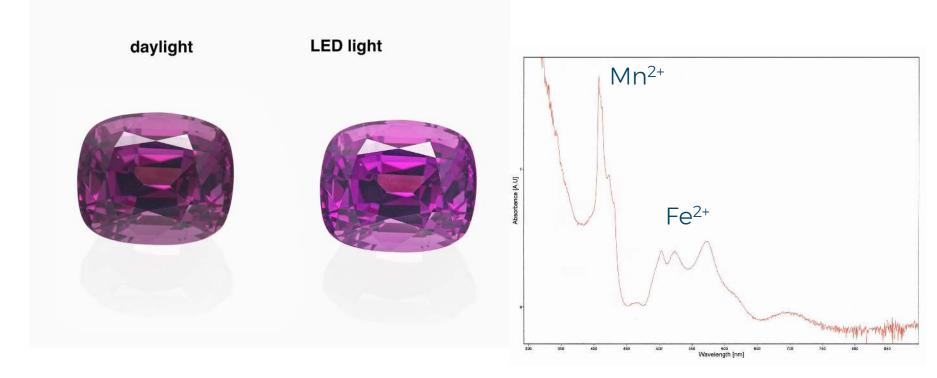
Pyrope garnets from Navajo Indian Reservation, New Mexcio USA.

rough stones brought to surface by ants digging in the soil, hence their name.



400 km 300 mile

Tanzanian Garnet with slight Colour Shift



Garnets from Tanzania with slight colour shift

Pyrope with distinct spessartine and low almandine component.



Colour Change Garnet from East Africa





Usambara effect: V-bearing colour change garnets from Tanzania.

Vanadium-bearing garnets of the pyrope-spessartine series may show a colour change and additionally an interesting Usambara effect.



Alexandrite vs Chrysoberyl





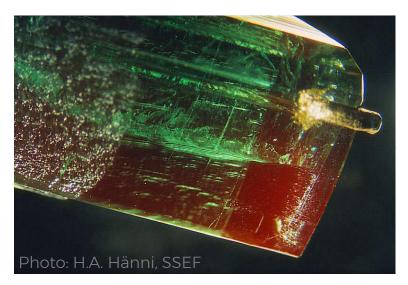
Alexandrite shows distinct pleochroism

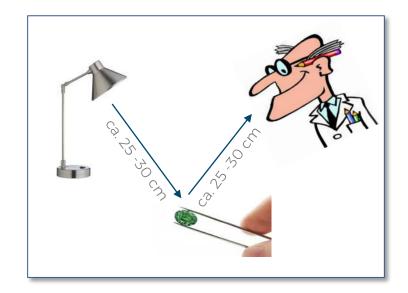
Alexandrite (LMHC) definition:

A chromium-bearing variety of chrysoberyl showing a colourchange in principle from a "cold" hue (e.g. greenish) in daylight to a "warm" hue (e.g. reddish-purplish) in incandescent light.

How to check for Colour Change

Do not hold the stone directly to a strong light source to check the colour change!





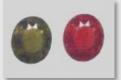
Emerald close to light source: not a colour change!

Colour change:

Change of **main hue** when holding the stone about 30 cm from the light source (standardised daylight and incandescent light). See also LMHC information sheet No. 9; www.lmhc-gemmology.org

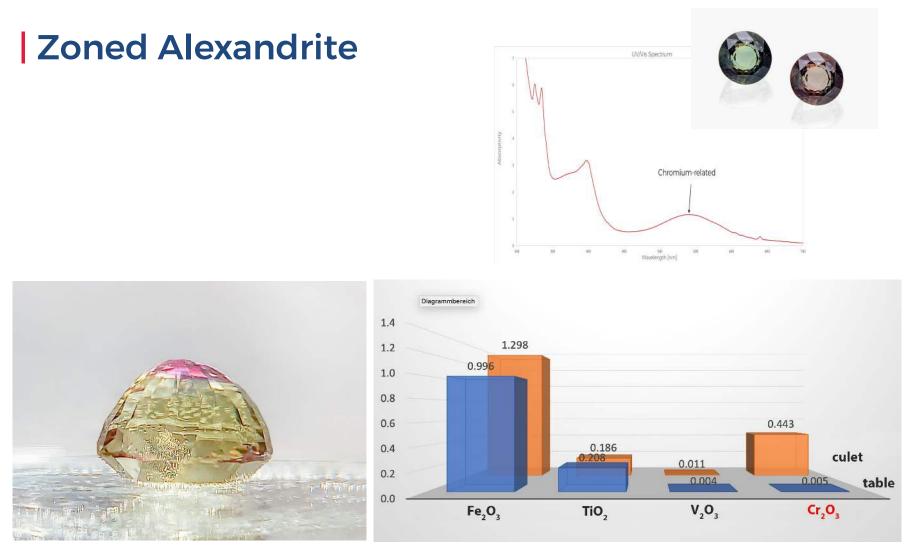


Alexandrite vs Chrysoberyl









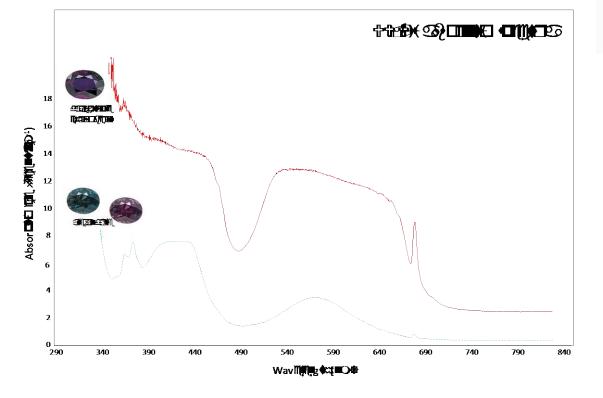
Chromium-rich zone at the culet (reddish) and chemical composition at table facet (blue bars) and culet (orange bars).

Photo: P. Lefèvre, SSEF



Not Alexandrite !





This chrysoberyl is only dark reddish purple.

Too much chromium (2.8 wt% Cr_2O_3) for colour change!

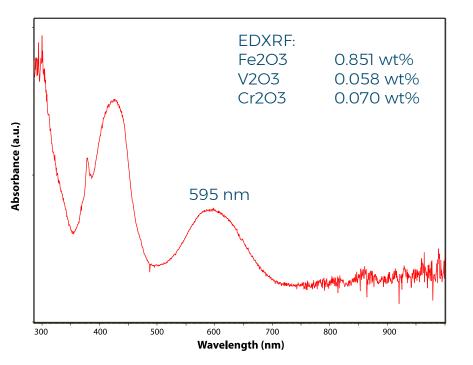


Not Alexandrite !

Chrysoberyl from Sri Lanka with equal vanadium and chromium concentration. The main absorption band is shifted to 595 nm.



No colour change effect !



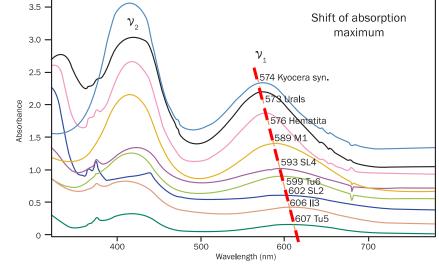
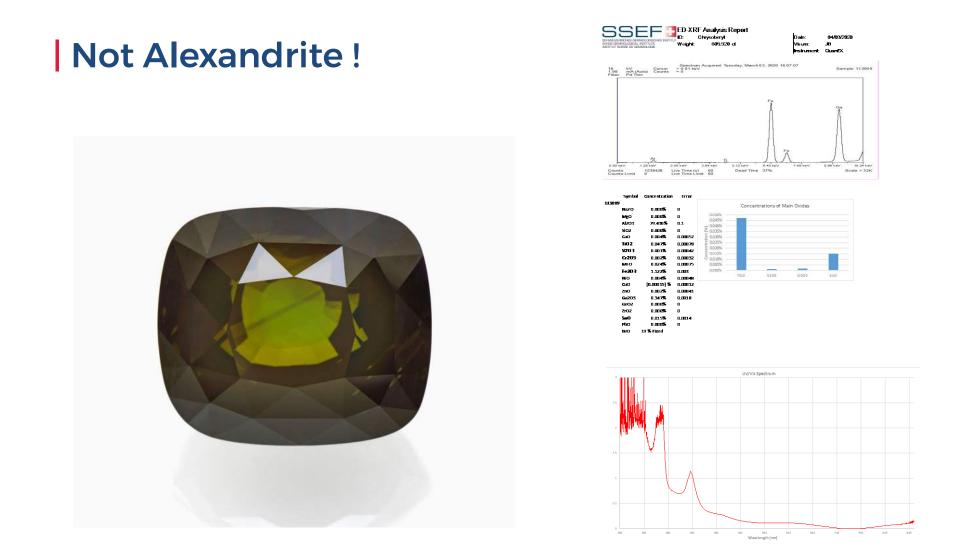


Figure 14: Non-polarized UV-Vis absorption spectra of V-bearing chrysoberyl from various sources (II Schmetzer, Krzemnicki, Hainschwang & Bernhardt, 2013

UV-Vis absorption spectra



Impressive chrysoberyl of **609 ct from Sri Lanka**. Only tiny traces of chromium (0.002 wt%) but much more iron. Consequently shows no alexandrite effect and by definition cannot be called alexandrite !



Vanadium-bearing Chrysoberyl





V-bearing chrysoberyl may show attractive bluish green colour but no colour change !

If iron is strongly dominating, then the colour shifts to olive green, thus similar to normal Fe-rich chrysoberyl.



LMHC meeting, December 2022 at SSEF





LMHC makes progress on laboratory report harmonization, discusses current challenges in detection of corundum treatments

BASEL: MARCH 14, 2023 – Holding its 30th meeting in Basel, Switzerland, the Laboratory Manual Harmonisation Committee (LMIC) has reported notable progress in the harmonisation of language used in laboratory reports. The participants in the meeting also discussed and shared new research findings on the treatments of genstones, and in particular corundum.

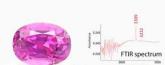
The LMHC meeting, which took place on December 5 and 6, 2022, was hosted by the Swiss Gemmological Institute SSEF.

The LMHC is currently comprised of representatives from the Central Gem Laboratory (CGL), CISGEM Laboratory, DSEF German Gem Lab, Gübelin Gem Lab, GIA Gem Laboratory, The Gem and Jewelry Institute of Thailand (GT) and the Swiss Gemnological Institute SSEF. The organisation is not formally connected to any trade organisation.

During the meeting, the LMHC members agreed to slight modifications on a number of their information sheets, which are formulated to facilitate better communication and understanding among professionals in the industry.

The main locus of the LMHC meeting was issues raised by treatments of corundum, including rubies and pink sapphires. These include the lowtemperature heating and irradiation.

In recent years, an increasing number of rubies and pink sapphires have come onto the market, after having previously undergone so called "low-temperature heating" (below 1000 °C), meant to



Heated pink sopphire with a characteristic FTIR spectrum. © LMHC.

slightly shift their colour to a better hue. Furthermore, as was reported in 2022, certain rubies and pink sapphres, some with a slightly purplish tint, have been treated by a limited number of individuals using radiotherapy equipment designed for cancer patients. This treatment can also induce a shift of the colour centre to a more attractive hue.

At the meeting in Basel, the LMHC labs decided to carry further research on these corundum treatments, in order to develop harmonised criteria for detecting their use.

https://www.lmhc-gemmology.org/s/LMHC-Press-Release-30th-meeting-report-14-3-202318.pdf



50 Years Swiss Gemmological Institute SSEF



Celebration marked by a symposium with key international speakers providing broad trade expertise and deep insights into mining, cutting, pearling, auctions, jewellery design and other themes.



All talks and a selection of photos of the event: https://www.ssef.ch/50years



50 Years Swiss Gemmological Institute SSEF















SSEF





| SGG Zentralkurs | June 2023 | PAGE 47

50 Years Swiss Gemmological Institute SSEF





Book published to celebrate the 50 year of SSEF.

To obtain a copy, please contact us (admin@ssef.ch).



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