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“Low temperature” heat treatment of Mozambique ruby - Results Report

*By Vincent Pardieu, Sudarat Saeseaw, Stanislas Detroyat, Victoria Raynaud, Supharart Sangsawong, Thitima Bhusrisom, Sasithorn Engniwat and Jonathan Muyal
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Figure 1: A ruby is heated at “low temperature” in air using the traditional blow pipe technique in Ratnapura (Sri Lanka). Photo: V. Pardieu © GIA

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Background

In May 2009, rubies from the Montepuez deposit in Mozambique appeared in the trade.

For more details about rubies from Mozambique, please see:
http://www.giathai.net/Mozambique_Ruby_Special_Issue.php
<http://www.gia.edu/gia-news-research-mozambique-montepuez-rubies>
and
<http://www.gia.edu/gia-news-research-mozambique-expedition-ruby-discovery-new-millennium>

Buyers of these rubies were initially from Thailand and African countries, however, buyers from Sri Lanka eventually became interested also.

Visiting Sri Lanka in 2013, it was heard that a gemstone heater from Beruwala (one of the main gem trading centers in Sri Lanka) was becoming well known for his expertise in heating rubies from Mozambique.



Figure 2: Master Simon, a blow pipe burner from Ratnapura (Sri Lanka) working on the heat treatment of some pink sapphires. Photo: V. Pardieu © GIA

Heat treatment of corundum in Sri Lanka has likely been performed on gems for near 1000 years or more as Teifaschi, an Arab writer wrote the following in 1240 (Sersen, 1991):

“In Serandib (Sri Lanka) and its environs, ruby is treated by fire. People take pebbles from the earth and crush and compress them into a mass with the aid of water. (This mixture) is daubed completely around a dry stone. Then, the whole thing is placed on a rock with other rocks set down around it. Dry firewood is thrown on the top, lit and blown upon (with bellows). The blowing is applied, along with more wood, till any black overtones on the ruby have disappeared.

The amount of fire and the application of wood depends on the extent of the blackness present. People know this by experience. They heat-treat stones for at least one hour and, at most, twenty days and nights. Then, they carefully extract the ruby, its blackness having disappeared.”

This description can be applied to the “blow pipe technique” we still can witness today in Sri Lanka (see Figure 1.) This technique is used to remove or partially remove some blue components in rubies and sapphires to give in the case of rubies the appearance of a purer hue. In the past it was also used to turn light blue sapphires colorless. Another particularly interesting description of that treatment is also given by James Emerson Tennent, an English traveler who wrote “Ceylon an account of the Island” in 1859:

“The blue tinge which detracts from the value of the pure ruby, whose colour should resemble “pigeon’s blood,” is removed by the Singhalese, by exposing the stone in the lime of a calcined shell and exposing it to high heat.”

This reference is to the best knowledge of the authors also one of the earliest mention of “Pigeon’s Blood” in the English literature.

A similar type of heat treatment of ruby to the ‘blow-pipe’ technique is also practiced in Vietnam and Thailand where a simple jeweler’s torch is used for few seconds or minutes and this is sometimes referred to as “snake bite” (see Figure 3 left). Usually only inclusion free stones are heated this way as included stones are likely to be damaged by the process. Generally the stone does not need to be repolished after this “snake bite” treatment.



Figure 3: Left: A burner heating some rubies with a jeweler torch (snake bite technique) seen in Vietnam (2005). Right: One of the Lakmini furnaces, developed in the 1980's, and commonly used in Sri Lanka to heat blue sapphires. Photos: V. Pardieu

Modern heat treatment in Sri Lanka.

The first modern furnace to be used in Sri Lanka is said to have been introduced by Bill Jewel, an Australian sapphire trader who sent the furnace to Naji Sammoon, a Sri Lankan gem merchant who had many connections in Hong Kong, Thailand and Australia and was helping Thai merchants to buy geuda sapphires (Terry Colham and Naji Sammoon Pers. Comm.). Since 1978 Naji Sammoon and his son Armil have been involved in the heat treatment of Sri Lankan pink sapphires, rubies and star rubies using an electric furnace where similar to the 'blow pipe' and 'snake bite' techniques. The main aim was to efficiently remove the blue component and thereby enhance the red or pink color of the gem.

Since then heat treatment technology became more understood in Sri Lanka. Sri Lankan made furnaces, like the Lakmini furnaces, were developed (see Figure 3 right) and many are used by local burners. With Sri Lankan merchants buying rubies and sapphires in many parts of Africa (Madagascar, Tanzania, Mozambique, Nigeria, Cameroon,...) many experiments happened since the 1980s and over the past 30 years some Sri Lankan burners developed a real expertise that can compete with what is done in Thailand. This expertise gives to the Sri Lankan buyers a noticeable advantage when they buy rough gems in the field.

Concerns over the identification of low temperature heated Mozambique rubies

In early January 2015 GIA became aware of some concern in the US market that Mozambique rubies were being heated in Sri Lanka at “low temperatures” and that laboratories were having difficulty in identifying this fact. This tallied with information given by Ashkar Ali Mubarak (left in Figure 4), a young gem merchant from Beruwala, who had earlier informed one of the authors, VP, that a “burner” in Beruwala had become very good at heating rubies from Mozambique. This success had lead many Sri Lankan merchants to become interested in Mozambique rubies.



Figure 4: Ashkar Ali Mubarak (left) and Mr. Fowsan (center) seen on January 21st 2015 in Beruwala, when we did the experiment. Photo: V. Pardieu © GIA

Having been informed about the “burner’s” identity and fame few weeks before, during GIA Field Expedition FE60 to Sri Lanka beginning Jan 10th 2015, VP began with a visit to Beruwala on Jan 11th to meet the “burner”; Mr. Fowsan (center in Figure 4) After meeting with him and with the help of Ali Ashkar Mubarak, Armil Sammoon and Mr. Punsiri Tennakoon, Mr. Fowsan agreed to carry out some heat treatment experiments for GIA and these were scheduled for Jan 21st 2015.

Mr. Fowsan related that he started his career working for another gemstone heater specializing in Sri Lankan pink sapphires, and then he moved his interest to Ilakaka pink sapphires, and started few years ago to work with rubies from Montepuez, Mozambique. His successful results with rubies from Montepuez became well known in 2014.

Materials and Methods

Samples:

Fourteen rough samples were selected to be fabricated as wafers. These fourteen were selected from a parcel collected onsite, during the GIA field expedition FE56 in Mozambique (September 2014). They are catalogued as C1 type. The area that they came from (*Mugloto*) is currently the most active ruby mining area around Montepuez. These samples were used in the initial heating experiments carried out in Sri Lanka. See Table 4 for details of the fabricated samples.

Table 1: Fabricated samples used in this paper, see also Table 2

GIA Reference # ¹	Wafer window orientation	Weight (carats)	Path length (mm)
10030993 5318	Perpendicular to the c-axis	0.737	1.602
10030993 5319	Perpendicular to the c-axis	0.774	1.605
10030993 5320	Perpendicular to the c-axis	0.780	1.456
10030993 5321	Perpendicular to the c-axis	0.692	1.026
10030993 5322	Perpendicular to the c-axis	1.469	1.883
10030993 5323	Perpendicular to the c-axis	1.244	1.871
10030993 5324	Perpendicular to the c-axis	1.167	1.441
10030993 5325	Parallel to the c-axis	0.607	0.925
10030993 5326	Parallel to the c-axis	0.680	1.035
10030993 5327	Parallel to the c-axis	0.459	0.895
10030993 5328	Parallel to the c-axis	0.323	0.871
10030993 5329	Parallel to the c-axis	0.412	0.899
10030993 5330	Non orientated	1.409	1.516
10030993 5331	Parallel to the c-axis	0.198	0.411

An additional three faceted samples were selected for additional heat treatment experiments in Bangkok for inclusions study only. These samples were mined in *Maninge Nice* area and ranged in weight from 0.289 to 0.317 see Table 2.

Table 2: Three faceted stones from the *Maninge Nice* mining area that were used in secondary heating experiments in Bangkok

GIA Reference #	Cut	Weight (carats)
10030516 4032	Pear Brilliant	0.293
10030516 4059	Marquise Brilliant	0.317
10030516 4073	Marquise Brilliant	0.289

Sample fabrication:

In this study, we selected fourteen samples (Table 1) for fabrication as optical wafers with two polished windows each. For seven samples the windows were oriented perpendicular to the c-axis while six other were parallel to the c-axis and one was fabricated to document inclusions and was not orientated. Accurate alignment of the samples for fabrication was assured by using GIA's Corundum C-Axis Device for Sample Preparation (Thomas. T., (2009))

¹ Note that throughout the paper only the last four digits of the sample control number are used to refer to a particular sample.

After heat treatment, thirteen samples were re-polished to remove burn marks before re-collecting data. Only sample 5324 did not need repolishing.

Sample photography and photomicrography:

The true color of the fourteen samples both before and after heat treatment were recorded using a Canon EOS 5D camera with a Canon Macro MP-E 65mm lens adapted to a purpose designed camera stand. Each wafer was photographed on both sides. In order to produce consistent results for each sample the photographs were taken under identical lighting conditions, each sample being placed on a Logan Electric Tru-View 810 Color Corrected Light Box (5000K lamp). A neutral density filter was used to calibrate the camera light box combination to produce a neutral gray. High-resolution reference photographs were then collected using transmitted light. As the reference photographs were taken of wafers with windows cut perpendicular or parallel to the c-axis, the color of the samples in the photographs taken using transmitted light can be considered representative of the color, of a nearly “pure o-ray” and a mixture of “o-ray and e-ray” respectively,

Photomicrographs of internal features were captured at up to 180 x magnifications with a Nikon SMZ 1500 system using darkfield, brightfield, diffused and oblique illumination, together with a fiber-optic light source when necessary. *Note:* The field of view information in the captions was calculated based on the magnification power of the microscope.

Infrared absorption (FTIR) spectroscopy:

Fourier-transform infrared (FTIR) spectroscopy was performed using a Thermo Nicolet 6700 FTIR spectrometer equipped with an XT-KBr beam splitter and a mercury-cadmium-telluride (MCT) detector operating with a 4x beam condenser accessory, and resolution was set at 4 cm^{-1} with 1.928 cm^{-1} data spacing. The spectra obtained were converted to absorption coefficient using $\alpha = 2.303A/d$ where “d” is the depth in centimeters. Each sample was scanned 2000 times.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS):

For chemical analysis, we used LA-ICP-MS technology with a Thermo Fisher Scientific iCAP Q Induced Coupled Plasma - Mass Spectrometer (ICP-MS) coupled with a Q-switched Nd:YAG Laser Ablation (LA) device operating at a wavelength of 213 nm. Laser conditions used 55 μm diameter laser spots, a fluency of around 10 J/cm^2 , and a 15 Hz repetition rate. 12 spots were analyzed on each wafer. For the ICP-MS operations, the forward power was set at $\sim 1350\text{ W}$ and the typical nebulizer gas flow was $\sim 0.80\text{ L/min}$. The carrier gas used in the laser ablation unit was He, set at $\sim 0.50\text{ L/min}$. The criteria for the alignment and tuning sequence were to maximize Be counts and keep the ThO/Th ratio below 2%. A special set of synthetic corundum reference standards were used for quantitative analysis. All elemental measurements were normalized on Al (internal element standard), this value approximates to the chemical composition of corundum.

The Heat treatment experiments:

All samples were studied to record their inclusions, infrared spectra and chemistry to compare the data obtained both before and after heat treatment. Two distinct sets of heating experiments were conducted:

Primary heating experiments carried out in Beruwala (Sri Lanka):

The primary heating experiments were carried out on Jan 21st 2015 in Beruwala (Sri Lanka) using the techniques of Mr. Fowsan (Figure 4) who preferred that their precise nature should not be revealed publically. Consequently certain elements of the experiments, while nevertheless witnessed by VP, may not be considered as scientifically useful as full access was not gained and accurate temperatures not made available. With this stated, it is assumed that Mr. Fowsan heat treated GIA's samples using the methods he would normally use on his clients stones and therefore the impact this process has on the color, inclusions, chemistry and infrared spectra is the same or similar to the effects recorded in the GIA specimens (see Table 1).

Objectives: To study the specimens both before and after this proprietary heat treatment process and see if it were possible to detect if the stones had been treated and if so record the necessary characteristics.

Two different heating processes were applied to the GIA samples by Mr. Fowsan:

Twelve wafers (see Table 4) were placed together in a 'crucible' and heated in air for "more than 1 hour" (using the "method Mr. Fowsan regularly uses on stones that have inclusions clearly present")

Two samples (5322 and 5324 (see Table 5)) were heated in air "for less than 1 hour" (using the "method Mr. Fowsan regularly uses on stones that were relatively free of inclusions")

Secondary heating experiments carried out in Bangkok (Thailand):

The secondary experiment was carried out in Bangkok with the support of Karim Gerchouche (from Premacut Ltd) and Dr. Laurent Massi.

Objectives: To verify the propositions detailed by Sudarat Seaseaw (Senior Manager of Colored Stones at GIA Laboratory Bangkok) and Mr. MTM Haris (gemologist at Emteem Gem Laboratory in Beruwala, Sri Lanka) that the appearances of the platelet inclusions commonly found in Mozambique rubies change after 'low temperature' heat treatment and if these changes could be used to confirm whether or not a Mozambique ruby has been heated.

This secondary heating process involved the use of an electric furnace operated in air (see Figure 5)



Figure 5: Left to right: Dr. Laurent Massi, Karim Guerchouche, Vincent Pardieu in the facility used for the secondary heating experiments. Photo © GIA

Three originally unheated faceted Mozambique rubies (see Table 2), selected for the presence of platelet type inclusions were submitted increasing temperatures for one hour at each step².

Table 3: The heat treatment steps applied to samples 4032, 4059, and 4073; three previously unheated faceted rubies from Mozambique

Date	Temperature °C	Time & conditions
Feb 11 th 2015	550	one hour in air
Feb 16 th 2015	650	one hour in air
Feb 19 th 2015	750	one hour in air

The inclusion scenes, with a focus on the platelets present were documented with photomicrography both before and after each of the heating steps of the treatment.

² It is intended to continue this experiment raising the temperature by 100 degrees each time until 1150 °c is reached as in many case stones are reportedly “warmed” in Bangkok up to 1100 °c.

Primary heating experiments carried out in Beruwala:

Color changes induced by the primary experiments in Beruwala

In the two samples illustrated in the selected (the clearest changes) images in Figure 6, and Figure 7, and the comprehensive listing in Table 4 and Table 5 we can see that the change in color before and after treatment is was not dramatic following the primary experiments but nevertheless it is in some cases clearly visible, i.e., the overall purplish areas were less visible after heat treatment. Note: It is likely that the difference in color may be more significant in the case of a faceted stone.

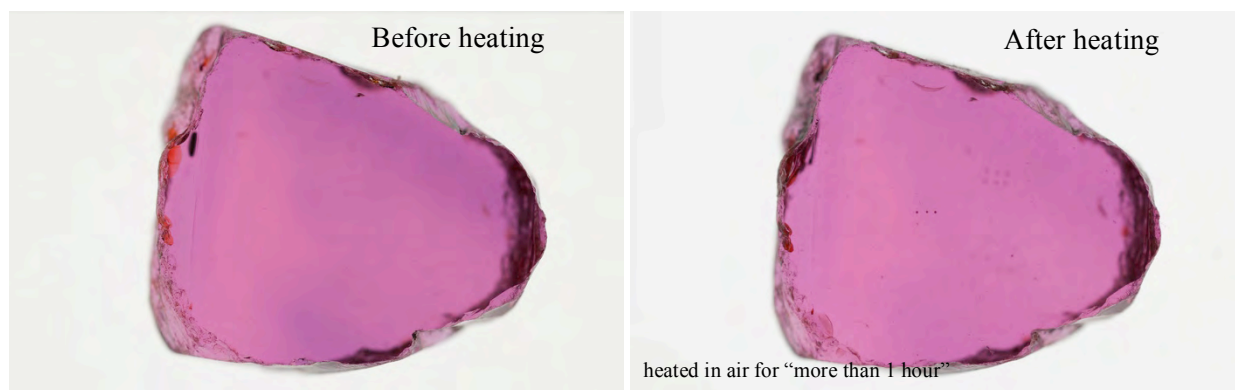


Figure 6: Sample 5323. Fabricated with window perpendicular to the c-axis. The color after heating is significantly less purple. Photos: S. Engniwat © GIA

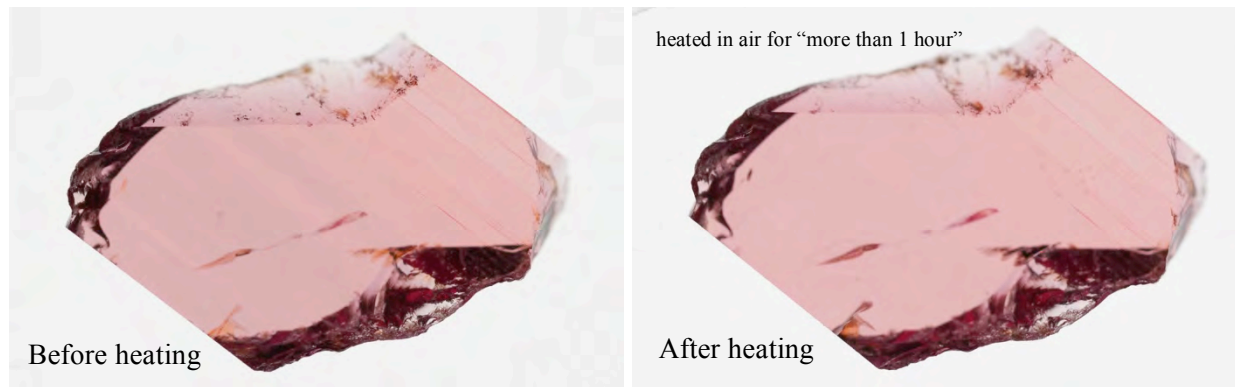
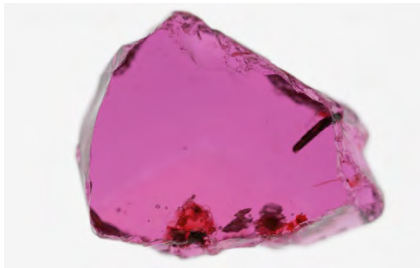
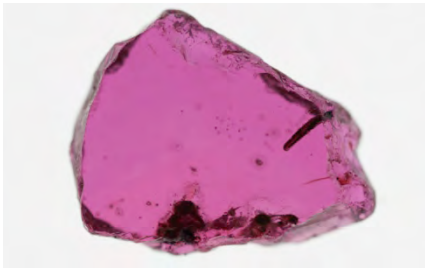
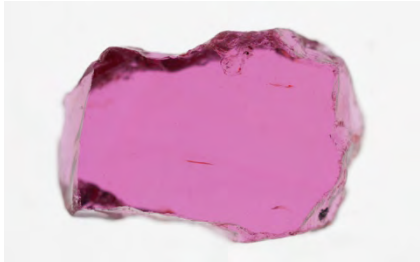
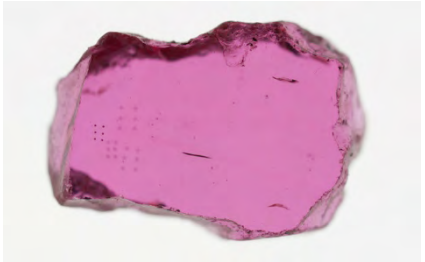
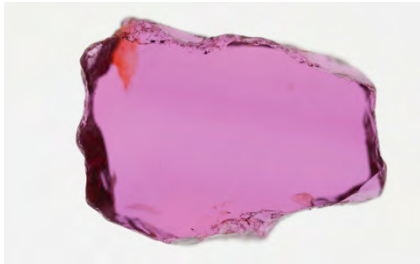
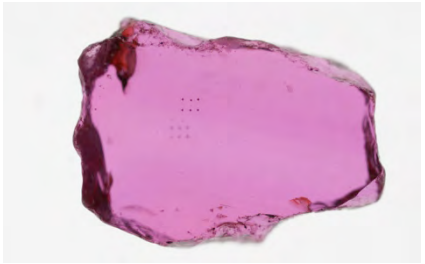
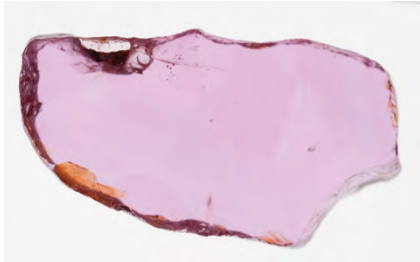
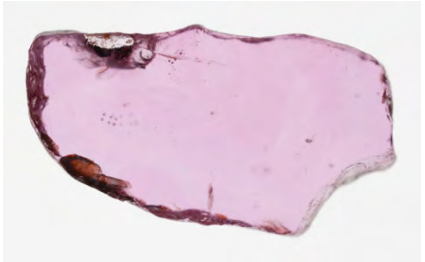
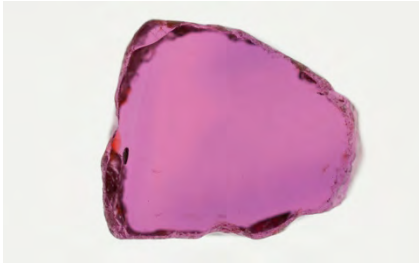
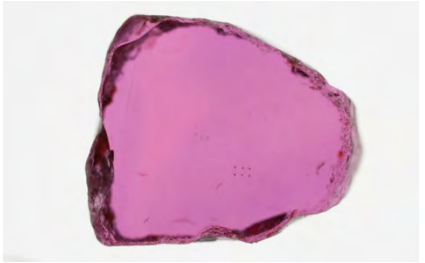
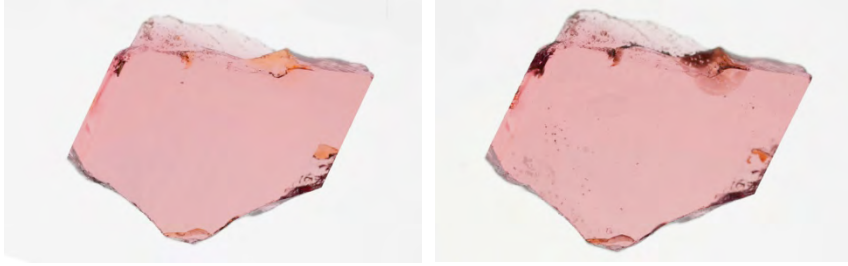


Figure 7: Sample 5328. Fabricated with window parallel to the c-axis. The color of the purplish bands after heat is significantly reduced and some change can be seen in the color of the iron stain filling in fractures. Photos: S. Engniwat © GIA

Table 4: Color changes induced in samples listed in Table 1 after more than one hour of Mr. Fowsan's 'crucible' heating process

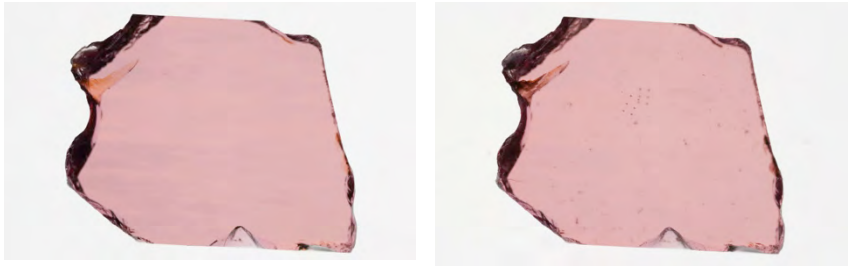
Reference #	Before heating	After Mr. Fowsan's 'crucible' heating	Notes
5318			Blue component to color clearly decreased after heating
5319			Blue component to color clearly decreased after heating
5320			Blue component to color clearly decreased after heating
5321			Blue component to color decreased after heating
5323			Blue component to color clearly decreased after heating

5325



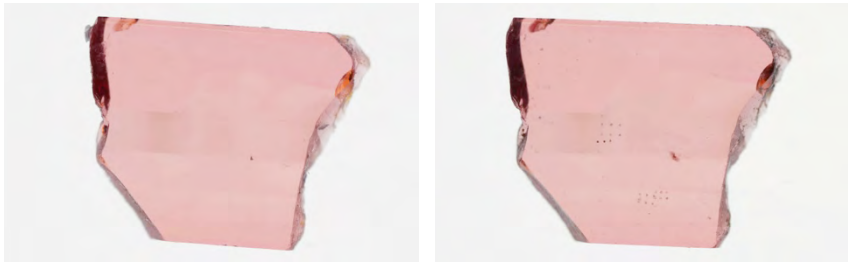
No perceptable change to the blue component however area of 'iron staining' has changed to a darker color (top right)

5326



Blue component to color decreased after heating

5327



No perceptable change to the blue component however area of 'iron staining' has changed to a darker color (bottom left)

5328



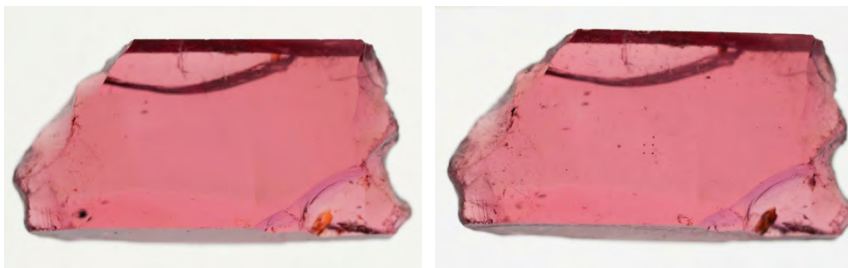
Blue component to color decreased after heating and areas of 'iron staining' have become darker.

5329



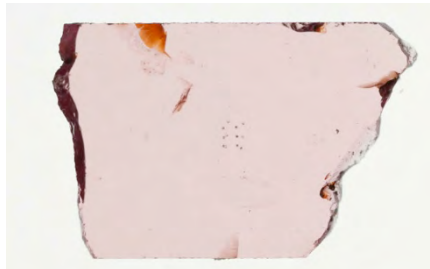
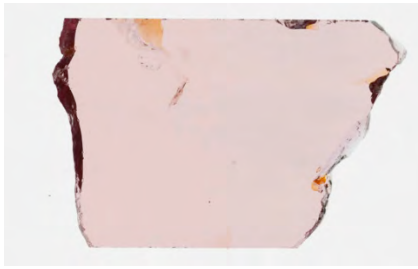
No perceptable change to the blue component however areas of 'iron staining' have changed to a darker color (bottom left and right)

5330



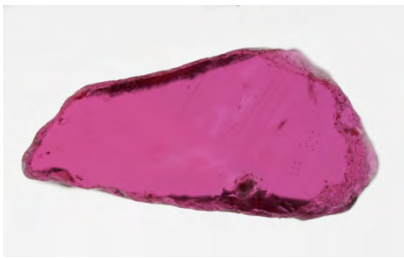
No perceptable change to the blue component

5331



Blue component to color decreased after heating and area of 'iron staining' has become darker (top left).

Table 5: Color changes induced in samples listed in Table 1 and after less than one hour of Mr. Fowsan's 'in air' heating process

Reference #	Before Heating	After Heating by Mr. Fowsan's 'in air' process	Notes
5322			Blue component to color decreased after heating
5324			Blue component to color decreased after heating

Changes induced to the appearance of inclusions during the primary heating experiments in Beruwela

In many cases following heat treatment during the primary Beruwela experiments there were consequences for mineral inclusions as discoids fracturing appeared around these inclusions. The larger crystal inclusions showing these consequences more clearly. However, not all the mineral inclusions seem to be impacted in the same manner: mica, feldspar and chalcopyrite inclusions appear more likely to be impacted than the amphibole or sillimanite inclusions.

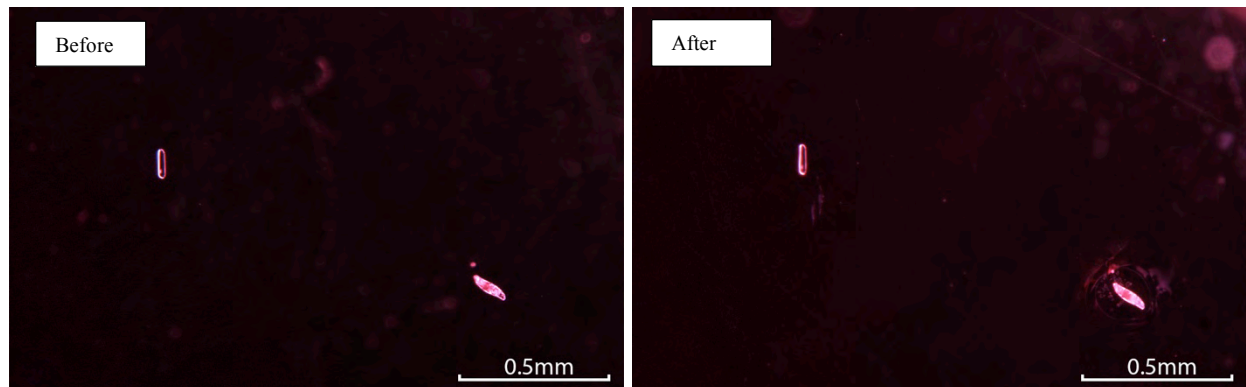


Figure 8: Sample 5318: Two crystals in a Ruby from Montepuez before (left) and after (right) heat treatment. On the left a transparent elongated crystal identified as amphibole group by Raman. The crystal of amphibole developed a slight associated tension fissure whereas the other inclusion (not identified) developed clear tension fissures. Dark field illumination magnified 64x. Photo: V. Raynaud © GIA.

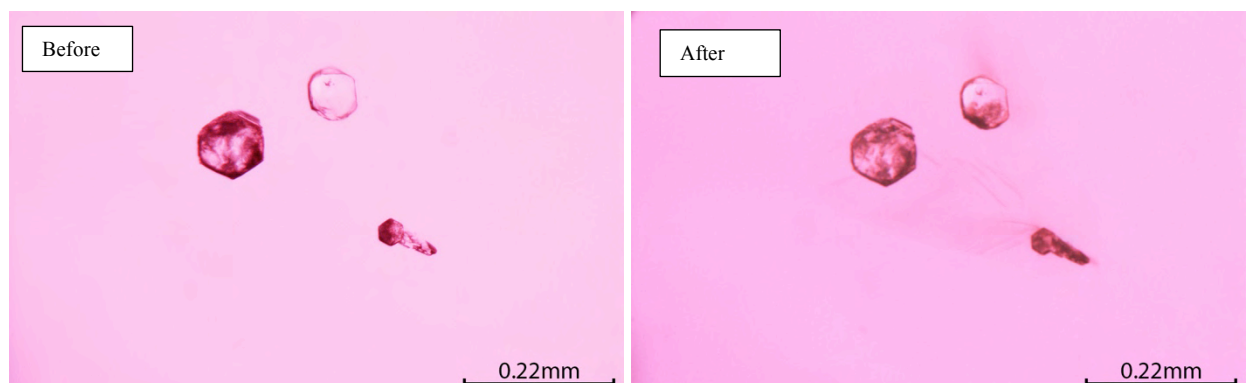


Figure 9 : Sample 5318: Three crystal before (left) and after (right) heat treatment. The 2 dark crystals were identified by Raman as mica while the colorless one was identified by Raman as feldspar. After the heat treatment experiment in Beruwala the crystals all developed associated fissures (not very visible in such lighting conditions). Diffuse light illumination, magnified 144x. Photo: V. Raynaud © GIA.

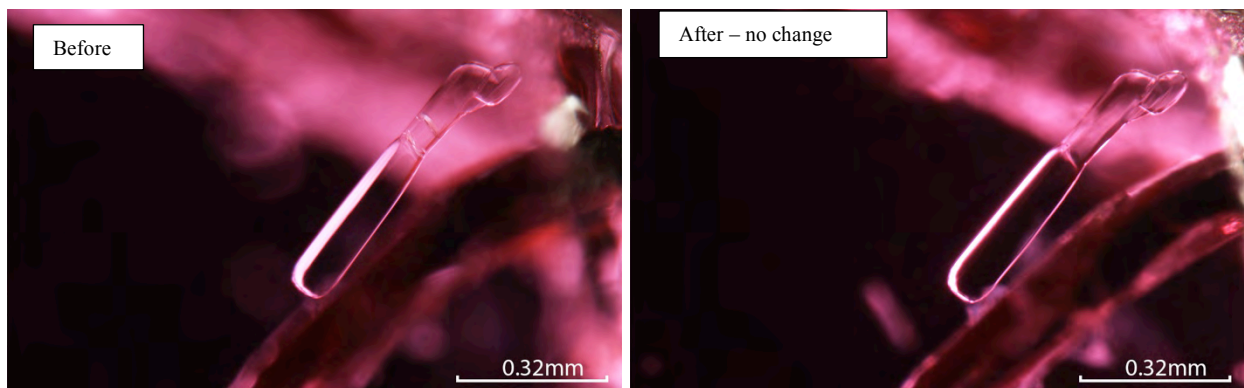


Figure 10: Sample 5318: Elongated transparent crystal (probably amphibole before (left) and after (right) the heat treatment experiment in Beruwala. No visible changes can be seen after the heat treatment experiment in Beruwala. Dark field illumination magnified 96x. Photo: V. Raynaud © GIA.

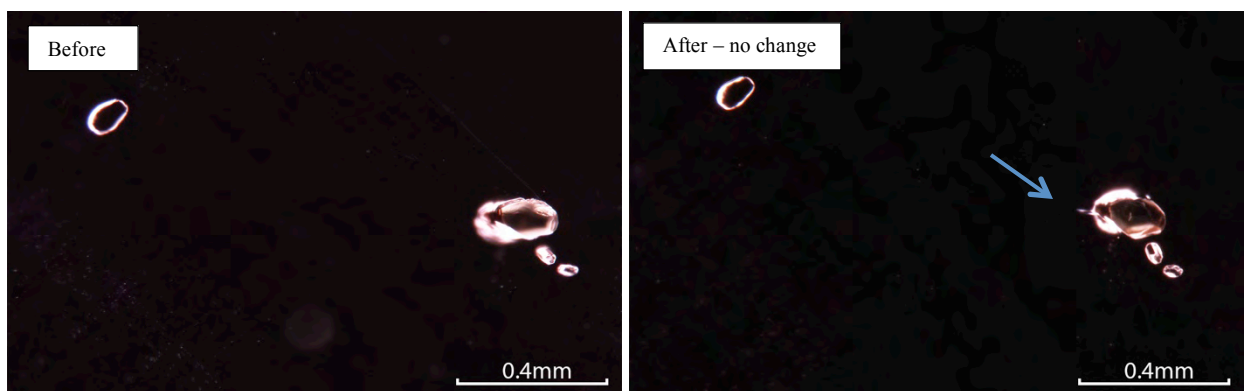


Figure 11: Sample 5321: Group of transparent amphibole crystals (identified by Raman) before (left) and after (right) heat treatment. The larger amphibole crystal developed a small tension fissure after heat treatment while the others remained intact. Dark field illumination magnified 80x. Photo: V. Raynaud © GIA.

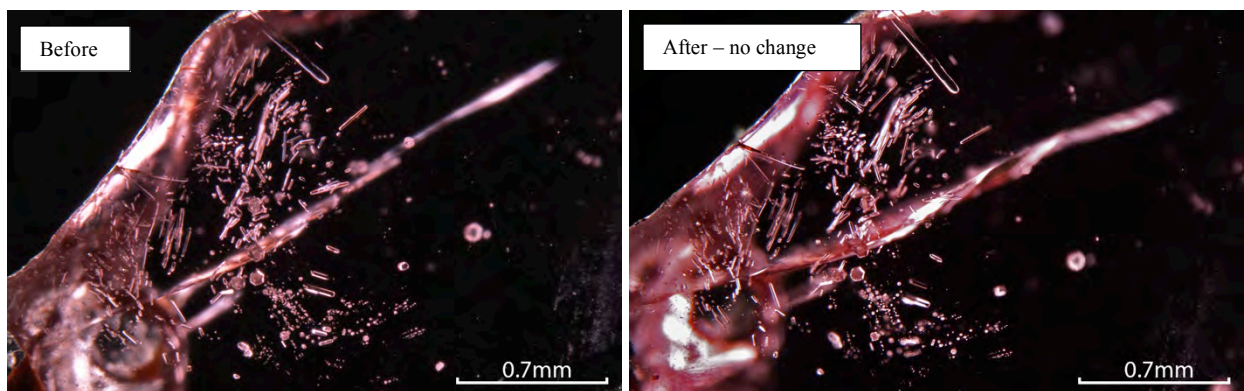


Figure 12: Sample 5321: Group of elongated transparent crystals as sillimanite and/or amphibole associated with hexagonal translucent mica crystals (all identified by Raman) before (left) and after (right) heat treatment in Beruwala. After the heat treatment experiment no changes are visible. Dark field illumination magnified 48x. Photo: V. Raynaud © GIA.

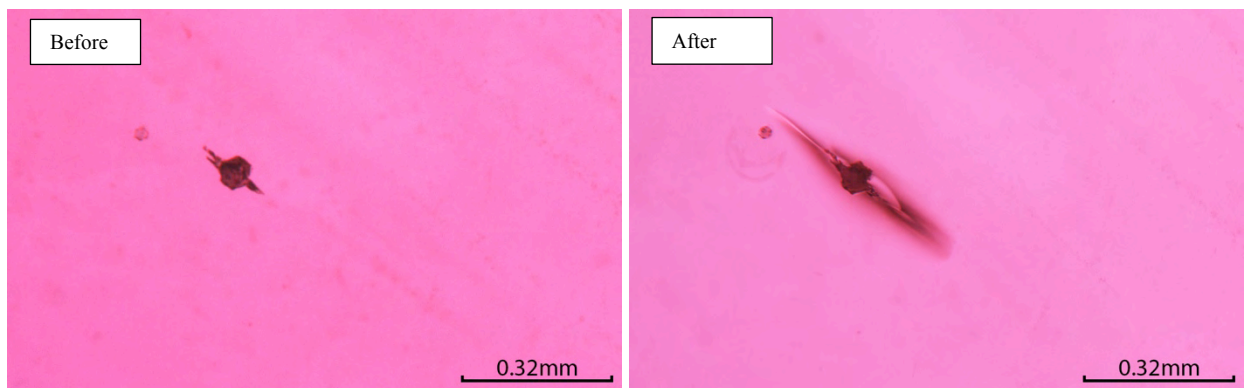


Figure 13: Sample 5322. Hexagonal crystals in unheated (left) and heated (right). Before heat treatment, the large crystal is associated with a frosted like tension fissure, a very common scene associated with mica crystals in unheated rubies from Montepuez. After the heat treatment experiment in Beruwala all the crystals developed associated tension fissures. Diffuse light illumination, magnified 96x. Photo: V. Raynaud © GIA.

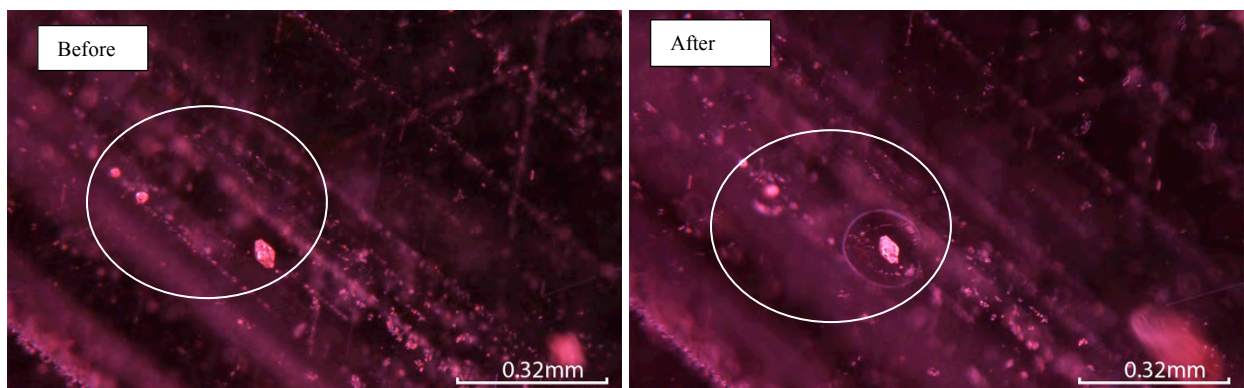


Figure 14: Sample 5322 before (left) and after (right) heat treatment in Beruwala. Before heat treatment some unidentified crystals are associated with parallel bands of whitish particles and thin needles. After heat treatment the larger crystals developed some classic tension fissures as seen in many heated stones. On the other hand no change is visible on the needles or particles. Dark field illumination magnified 96x. Photo: V. Raynaud © GIA.

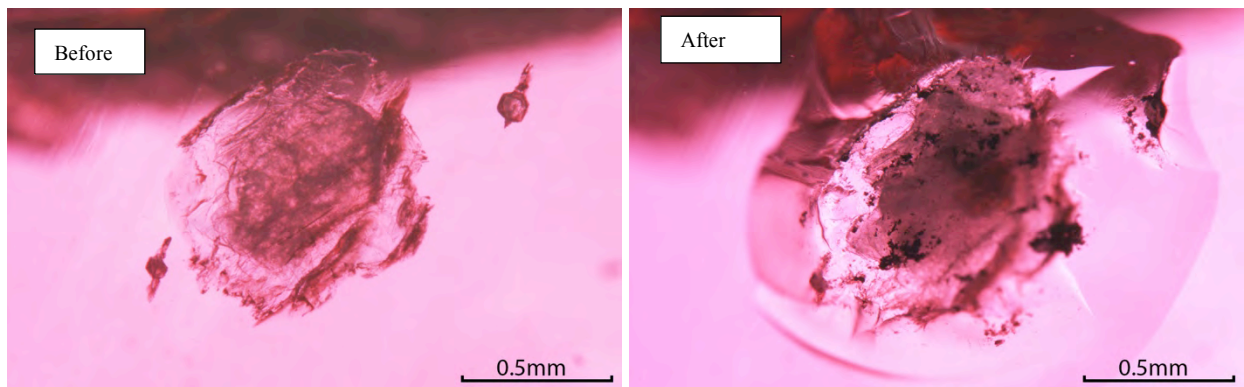


Figure 15: Sample 5322 before (left) and after (right) heat treatment in Beruwala. Before heat three hexagonal, translucent crystals (identified as mica using Raman) can be seen associated with their characteristic frosted like fringes. After the heat treatment experiment in Beruwala, the larger crystal developed some large fissures reaching the surface of the stone. The crystal on the right was removed by repolishing as it was very close to the surface and finally the small mica crystal on the left looks unaltered. Diffuse light illumination magnified 64x. Photo: V. Raynaud © GIA.

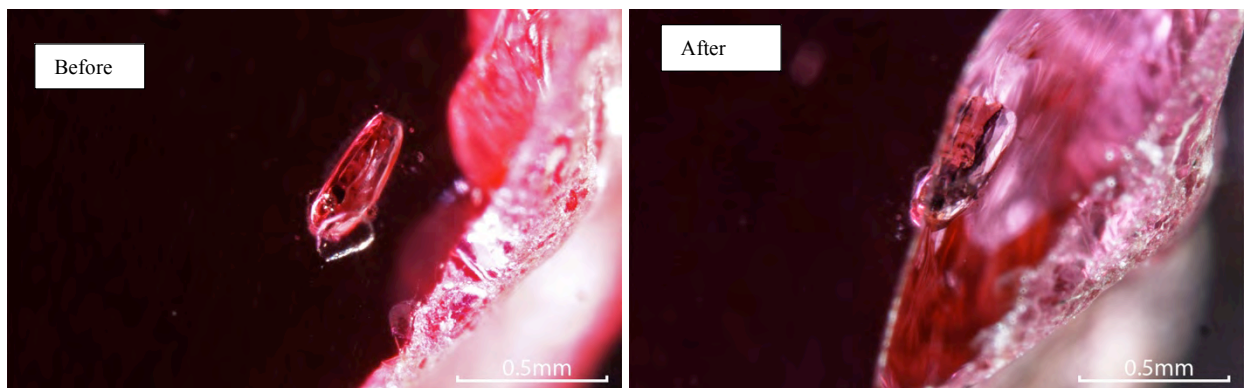


Figure 16: Sample 5323 before (left) and after (right) heat treatment in Beruwala: Before heat treatment a large crystal inclusions can be seen close to the surface of the sample. After heat treatment a large fissure developed around the crystal. Dark field illumination + fiber optic light magnified 64x. Photo: V. Raynaud © GIA.

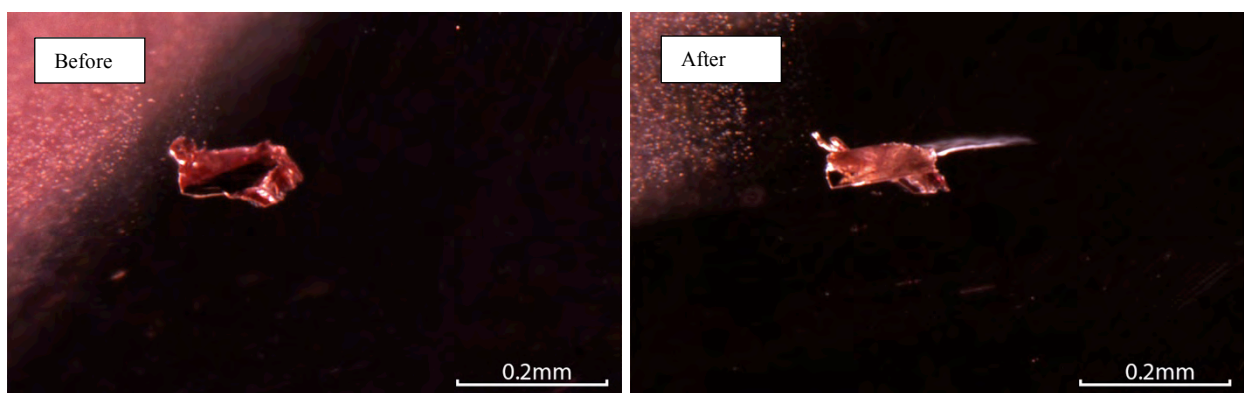


Figure 17: Sample 5329 before (left) and after (right) heat treatment experiment in Beruwala: Unidentified crystal associated with particles. After heat treatment experiment in Beruwala the crystal was here partially removed by repolishing as it was close to the surface. Some associated tension fissures appeared around the crystal. Dark field illumination magnified 160x. Photo: V. Raynaud © GIA.

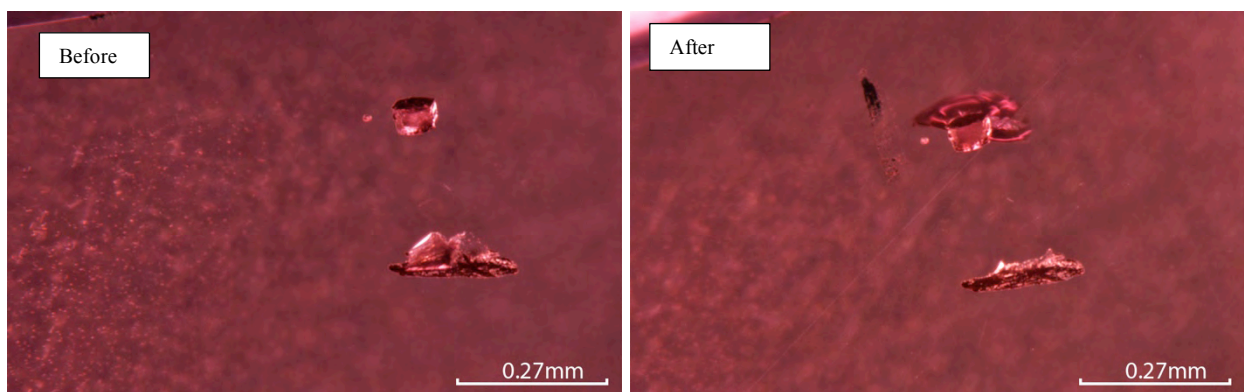


Figure 18: Sample 5330 before (left) and after (right) heat treatment in Beruwala. Before heat, a large hexagonal looking crystal is associated with smaller one and minute particles. After heat treatment some associated tension fissures appeared around the large hexagonal crystal while the crystal in the lower part of the photo was mostly removed during the repolishing process. Dark field illumination magnified 112x. Photo: V. Raynaud © GIA.

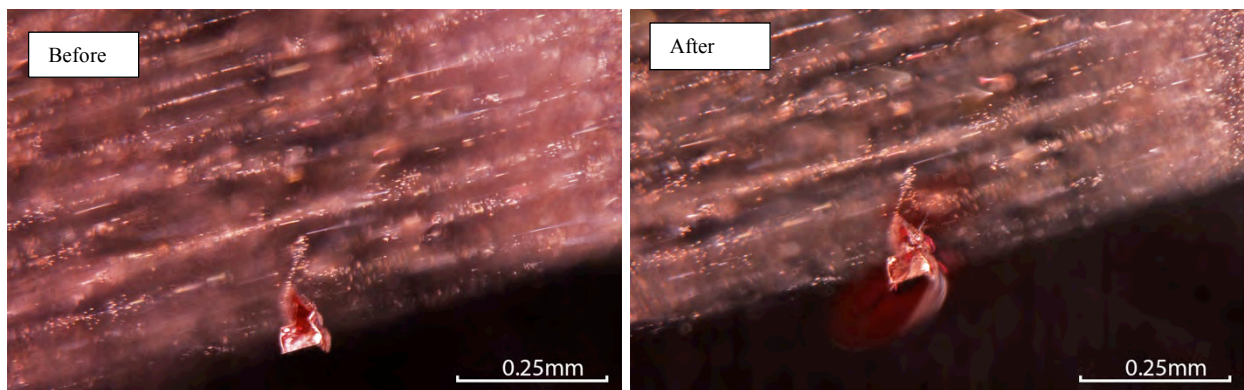


Figure 19: Sample 5327 before (left) and after (right) heat treatment experiment in Beruwala. Before heat an unidentified whitish crystal with small tension fissure is visible associated with particles. After heat treatment the crystal developed a large associated tension fissure while the particles remained unchanged. Dark field illumination magnified 128x. Photo: V. Raynaud © GIA.

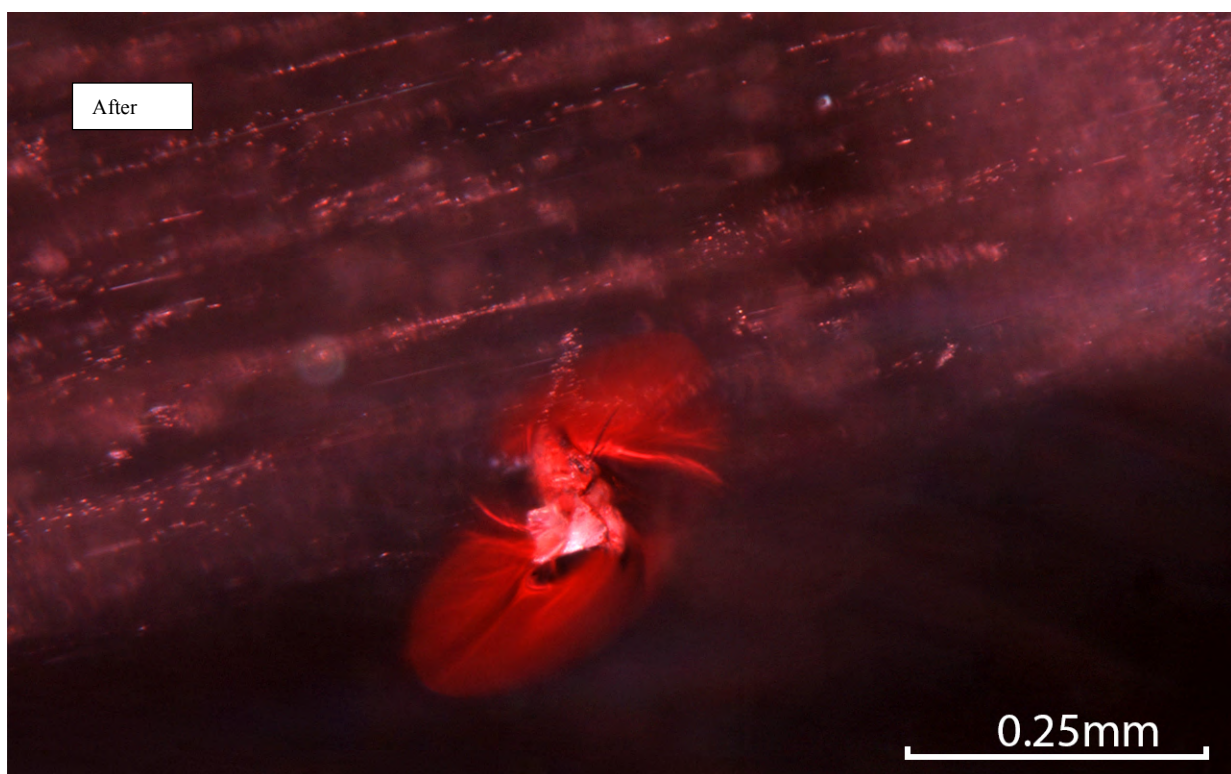


Figure 20: Sample 5327. Another view of that large associated tension fissure developed after the heat treatment experiment. Fiber optic light illumination magnified 128x. Photo: V. Raynaud © GIA.

Besides changes to mineral inclusions some alterations were also noted to the appearance of surface reaching fissures in-so-much-as the limonite / iron staining if present became darker. When observed in diffused light the limonite / iron staining changed from a bright orange before heating to a dark brown after heating. Furthermore the fractures commonly became more granular and whitish in appearance after heat treatment.

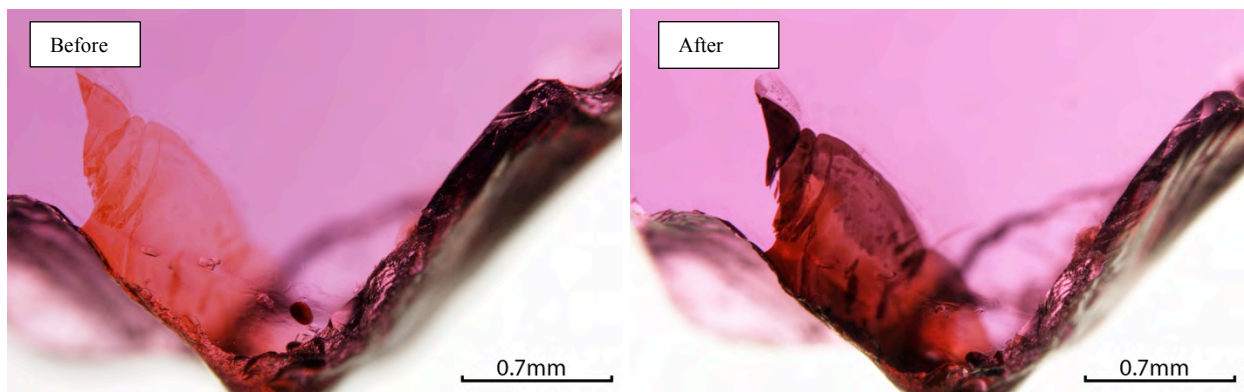


Figure 21: Sample 5320 before (left) and after (right) heat treatment in Beruwala: Before heat treatment we can see three transparent unidentified crystals and one opaque one, associated with an associated surface reaching fissure filled with an orange foreign substance (probably limonite or iron stain) after heat treatment and repolishing the transparent crystals did not change, the opaque one was cut off during the repolishing process, but the orange heal fissure became darker after treatment. Diffuse light illumination magnified 48x. Photo: V. Raynaud © GIA.

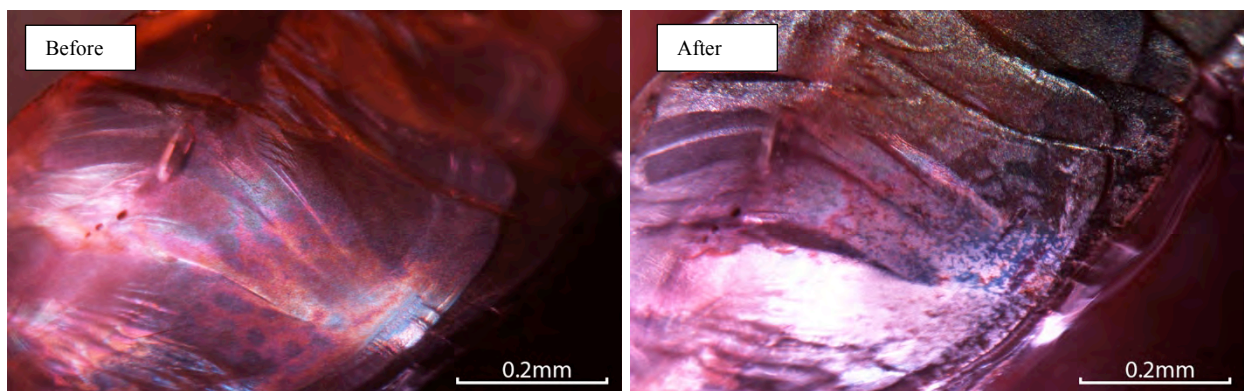


Figure 22: Sample 5320 before (left) and after (right) heat treatment in Beruwala. Here we can see a close up on the same surface reaching fissure as on the previous photos but using a different lighting method. Before heat treatment some iridescent color patches can be seen using fiber optic illumination after heat treatment the aspect of the fissure changed: The iridescence is more like a “dots” of colors, some whitish and dark areas appeared and finally the fracture extended a bit. Fiber optic illumination magnified 144x. Photo: V. Raynaud © GIA.

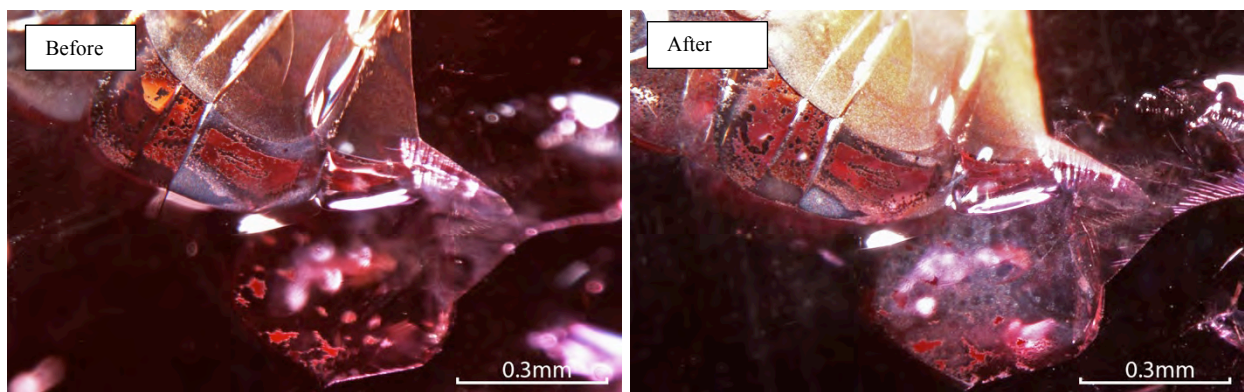


Figure 23: Sample 5331, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see an surface reaching fissure showing some dry orangey iron stain like residues in. After heat treatment the aspect of the fissure is less transparent now as some whitish granular features appeared in most of the stone. In fact despite the fact that the upper part of the fracture appears lighter in color compared to the previous photo, the iron stain like residues present in the fissure look actually darker after heat treatment (as we can see on color calibrated photos). Fiber optic light illumination magnified 96x. Photo: V. Raynaud © GIA

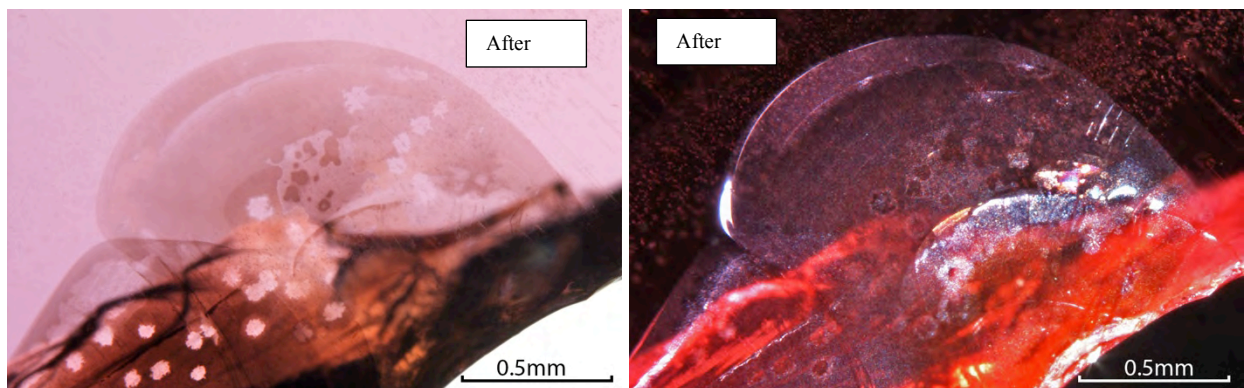


Figure 24: Sample 5325 after heat treatment in Beruwala using two different lighting methods (Diffuse light illumination on the left and fiber optic light illumination on the right). Note: Before heat treatment the fissure was nearly invisible. The aspect of the fissure looks granular with whitish and brownish residues filling unevenly the fracture. Magnification 64x. Photo: V. Raynaud © GIA.

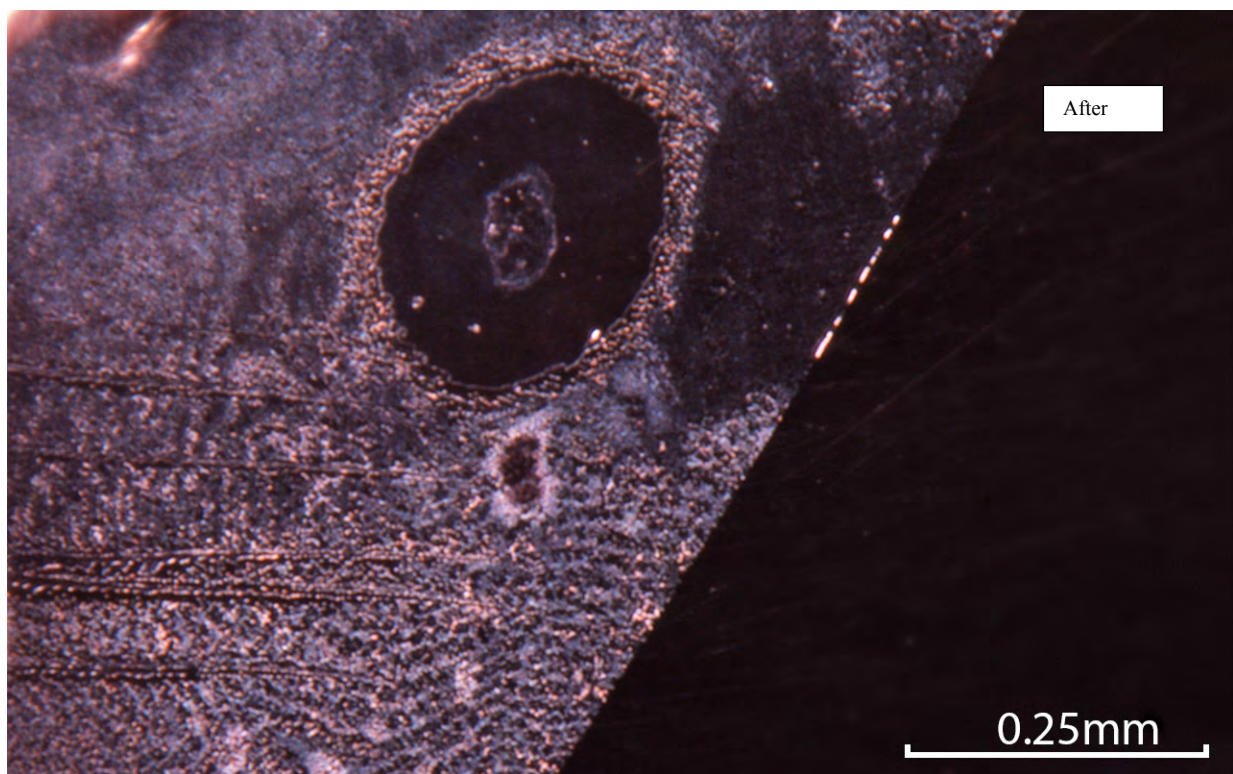


Figure 25: GIA reference number 5329 after heat treatment: Details on a whitish looking surface reaching after heat treatment. Dark field illumination magnified 128x. Photo: V. Raynaud © GIA.

The aspect of some healed fissures were also altered in so much as secondary fissures developed around the negative crystals comprising the healed fissures, however, this was not noted in every instance:

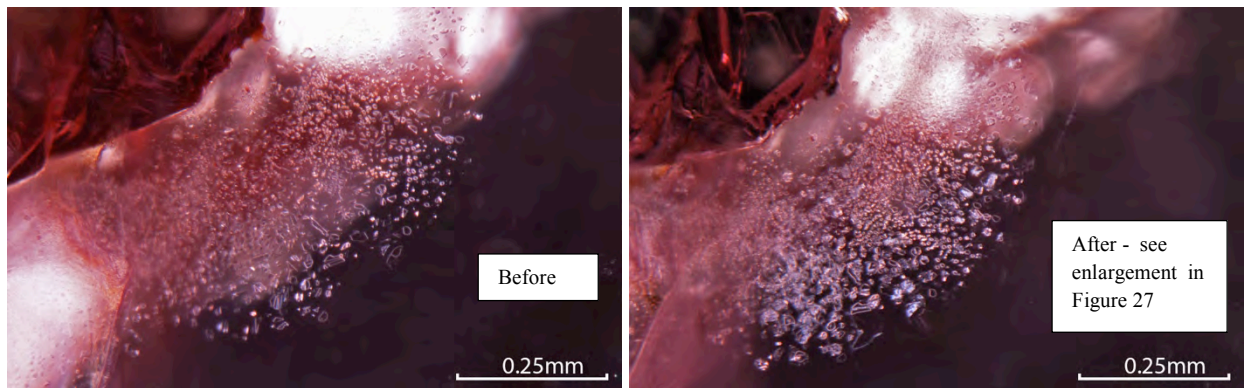


Figure 26: Sample 5321, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see a plane of small flat negative crystals. After the heat treatment the negative crystals comprising the healed fissure are now associated with numerous tension halos and show a whitish aspect. Dark field illumination magnified 128x. Photo: V. Raynaud © GIA.

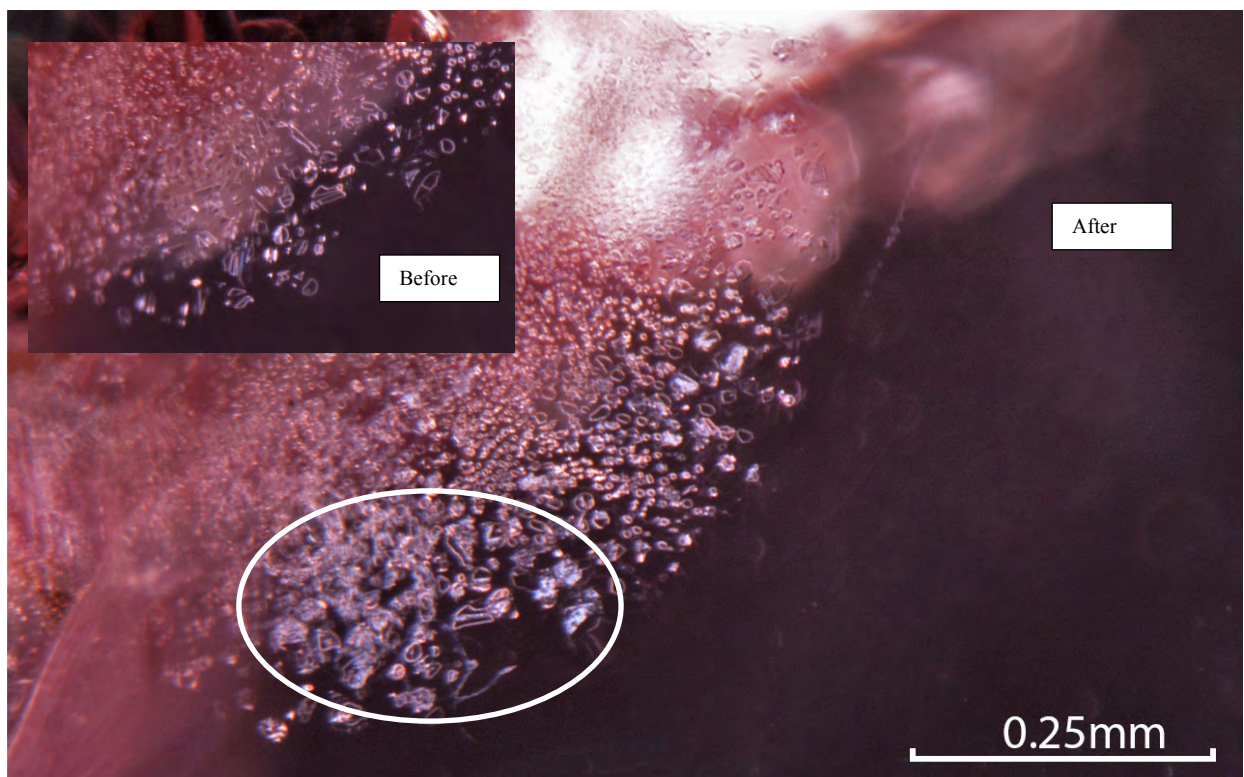


Figure 27: Sample 5321, after the heat treatment the negative crystals comprising the healed fissure are now associated with numerous tension halos and show a whitish aspect. Dark field illumination magnified 128x. Photo: V. Raynaud © GIA

No significant changes were noted in the aspect of the needle inclusions or the bands of ‘particles’ on our orientated wafers. However, the fabrication process does not provide specimens’ way to study the iridescence on the surface of needles and platelets as these platelets are parallel or perpendicular to the window which is also acting also as a mirror:

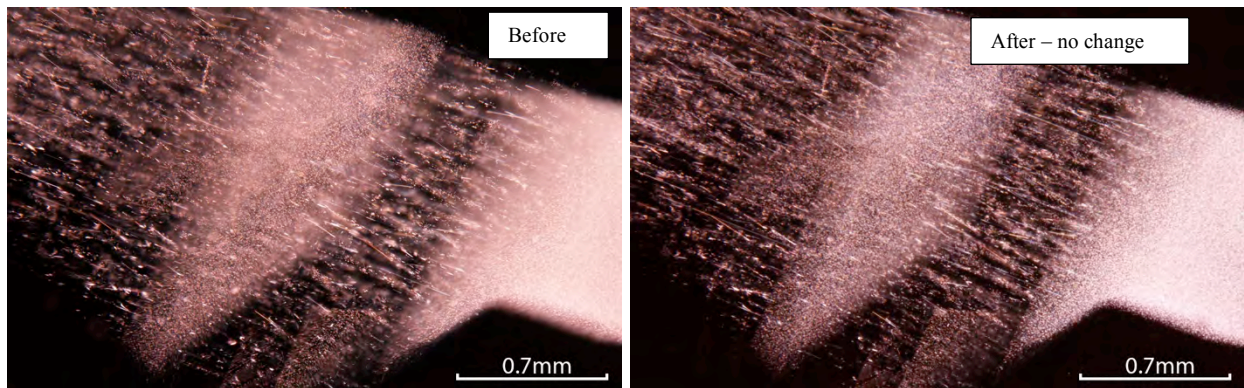


Figure 28: Sample 5327, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see needles associated with particles. After heat treatment no significant changes are visible. Dark field illumination magnified 48x. Photo: V. Raynaud © GIA.

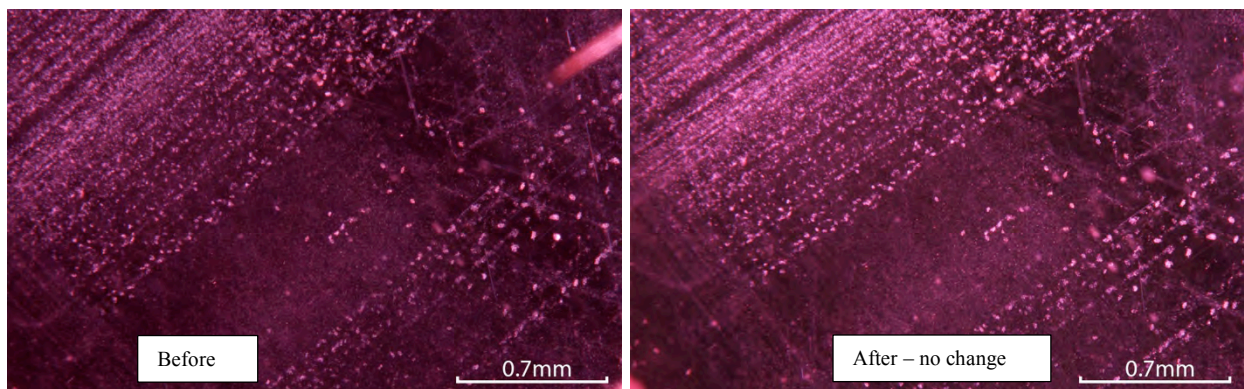


Figure 29: Sample 5319, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see some parallels bands of whitish. After the heat treatment no visible changes are noticeable. Dark field illumination magnified 48x. Photo: V. Raynaud © GIA.

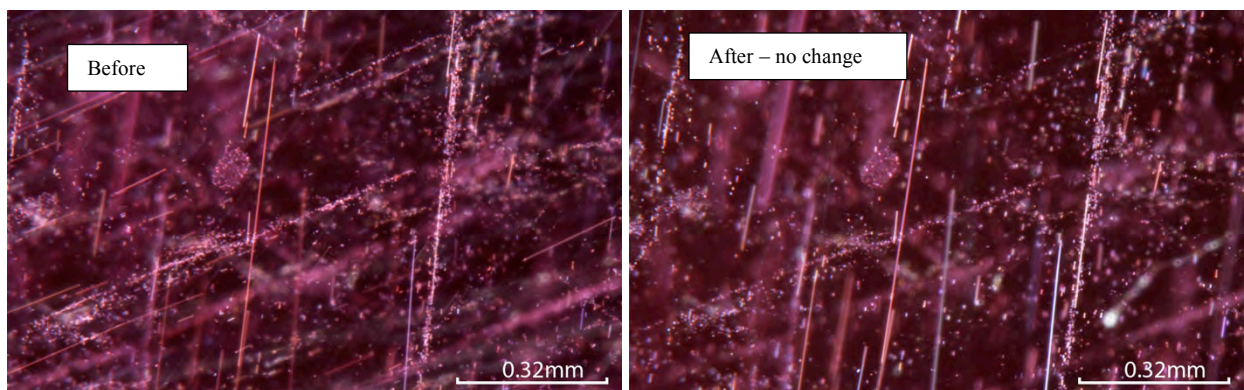


Figure 30: Sample 5323, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see some iridescent thin needles, low density bands of minute particles and flake like particles. After heat treatment no changes are visible. Fiber optic light illumination magnified 96x. Photo: V. Raynaud © GIA.

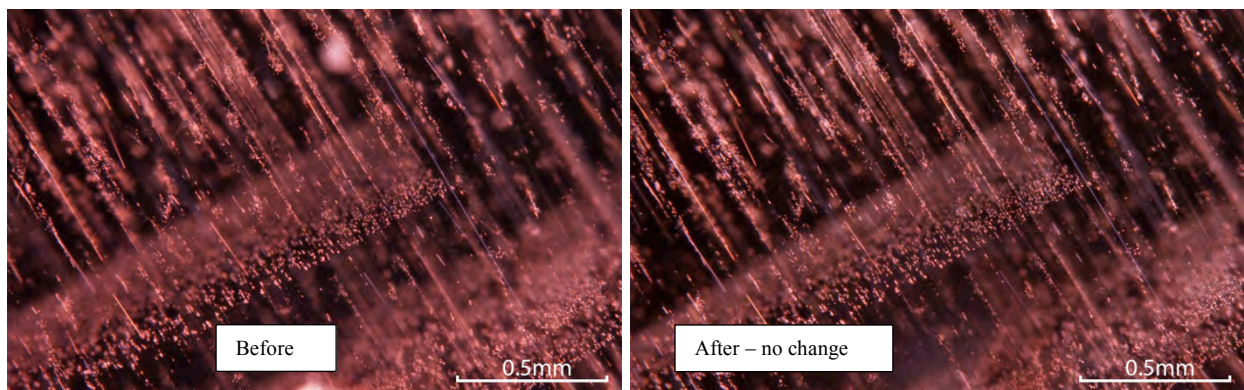


Figure 31: Sample 5325, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see some bands of particles associated with needles intersecting planes of minute particles. After heat treatment no significant changes are visible. Dark field illumination magnified 64x. Photo: V. Raynaud © GIA.

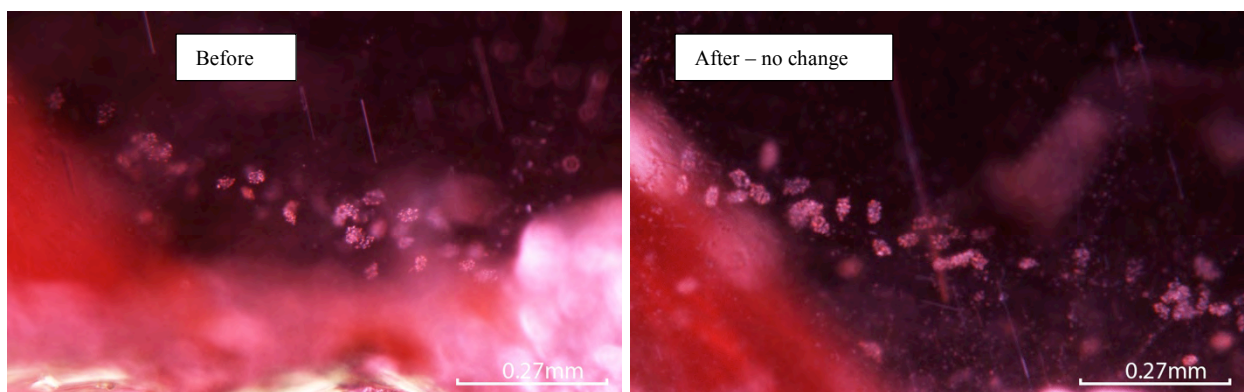


Figure 32: Sample 5319, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see some clouds of minute whitish particles associated with needles. After heat treatment: Once again there is no visible change. Dark field illumination magnified 112x. Photo: V. Raynaud © GIA

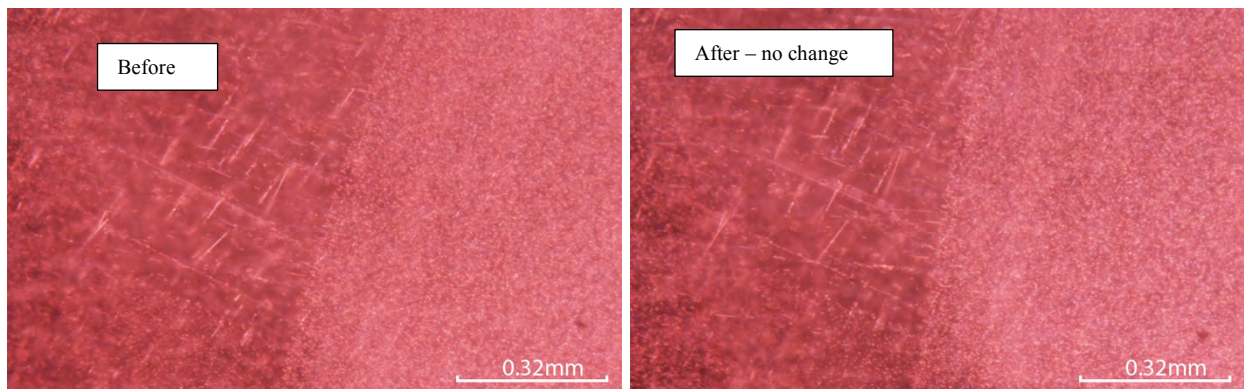


Figure 33: Sample 5330, before (left) and after (right) heat treatment in Beruwala. Before heat treatment we can see bands of whitish minute particles associated with needles. After heat treatment in no changes are visible. Diffuse light illumination magnified 96x. Photo: V. Raynaud © GIA.

GIA gemologists working at the Bangkok lab on Mozambique rubies submitted by clients noticed that in some cases the surface of some platelets seemed altered in comparison with previous observations of these types of inclusions. The surface of the platelets appeared regularly “spotted”, “deteriorated” or “stained”. Similar observations were also made by Mr. MTM Haris, a gemologist from Beruwala (Sri Lanka) who is well experienced with this material. In both instances it had been theorized that this change in the appearance of the platelets may be due to the heating process.

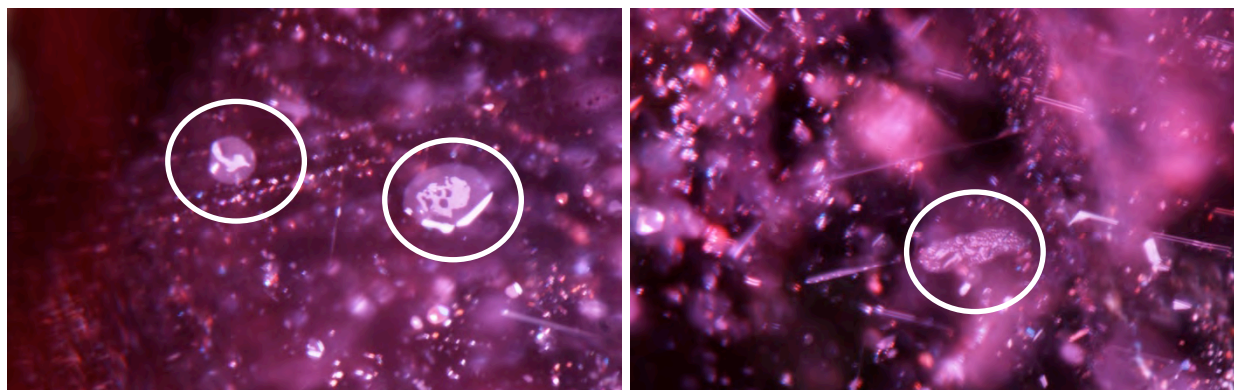


Figure 34: Sample 100305164763 from GIA’s collection of known heated Mozambique rubies that were said to have been heated at around 1,000°C – not used in these experiments. . That stone was known to have been heat treated reportedly around 1000 degrees in air for few hours in Chanthaburi (Thailand). Some whitish spots or tarnishing are clearly visible on the surface of several platelets. Fiber optic light illumination magnified 180x. Photo: J. Muyal © GIA.

As the surface of the included platelets cannot easily be seen on samples fabricated as wafers, further experiments were arranged using unheated faceted Mozambique rubies (Table 2).

Secondary heating experiments carried out in Bangkok.

In the secondary heating experiment three unheated faceted Mozambique rubies (Table 2) were specifically selected for their inclusions and more particularly the presence of platelets that could easily be seen. Each stone was heated in air three times consecutively, firstly at 550°C then at 650°C and finally at 750°C with examinations of the stone and its inclusions taking place at each stage of the process. After heating to 750°C it was noted that the surface of some, but not all, of the platelets changed; Some spottiness, staining or deterioration appeared on the surface of some platelets and this appeared to be similar to the observations made when viewing the platelets seen in Mozambique rubies (from the GIA reference collection) that were assumed to have been heated to 1100°C in air for a short period of time (stated by the supplier).

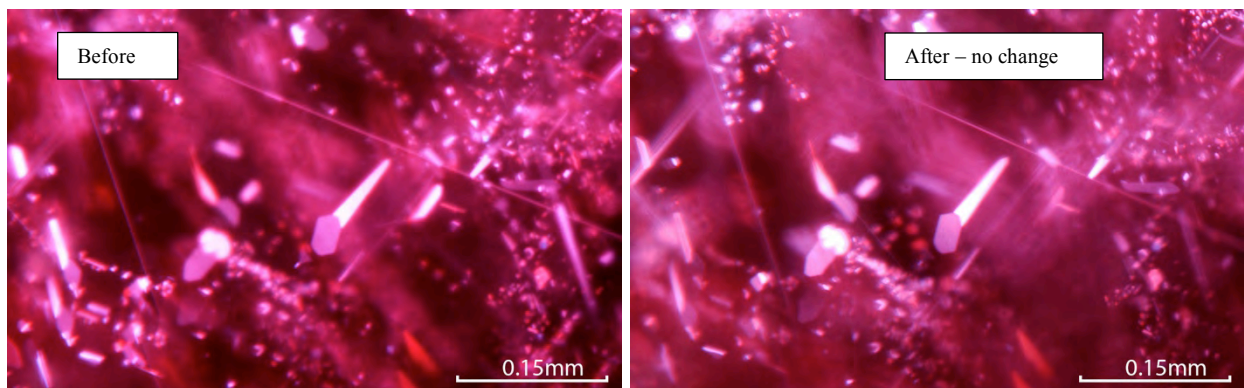


Figure 35: Sample 4032, before (left) and after (right) heat treatment in Bangkok. Before heat treatment we can see highly reflective platelets and needles. After heat treatment experiment in Bangkok (the stone was heated 3 times at 550°C, 650°C and 750°C) no visible changes can be seen. Fiber optic light illumination magnified 200x. Photo: V. Raynaud © GIA.

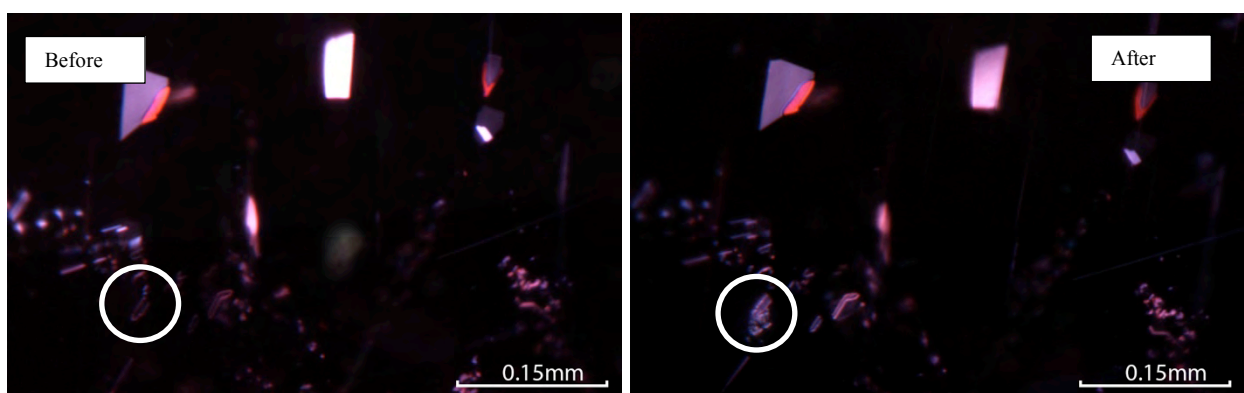


Figure 36: Sample 4073, before (left) and after (right) heat treatment in Bangkok. Before heat treatment we can see highly reflective iridescent and few needles. After heat treatment experiment in Bangkok (the stone was heated 3 times at 550°C, 650°C and 750°C) no visible changes can be seen except for one small platelet in the lower left part of the photo (circled). Fiber optic light illumination magnified 200x. Photo: V. Raynaud © GIA.

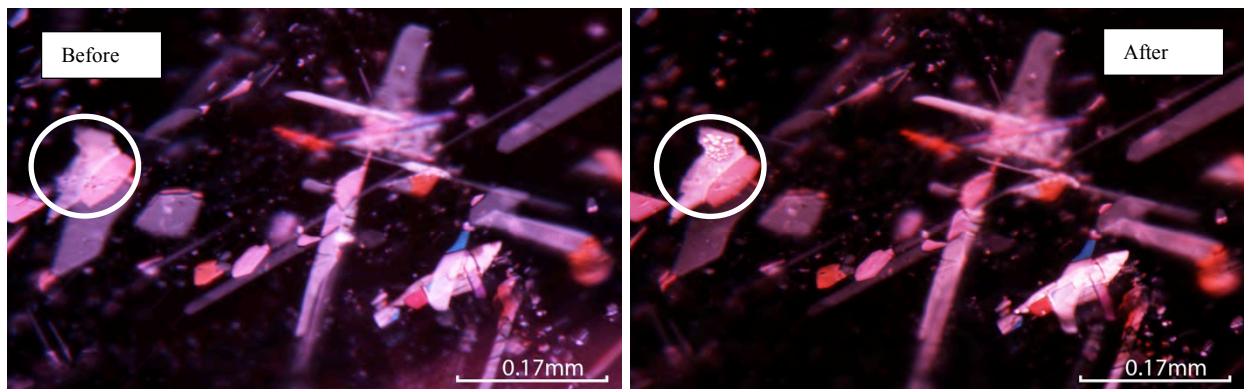


Figure 37: Sample 4073, before (left) and after (right) heat treatment in Bangkok. Before heat treatment we can see highly reflective iridescent platelets and few needles. After heat treatment experiment in Bangkok the stone was heated 3 times at 550°C, 650°C and 750°C) on the main platelet on the left several bright spots are now visible on the platelet. No other spots are visible on any other platelets in this image. Fiber optic light illumination magnified 180x. Photo: V. Raynaud © GIA.

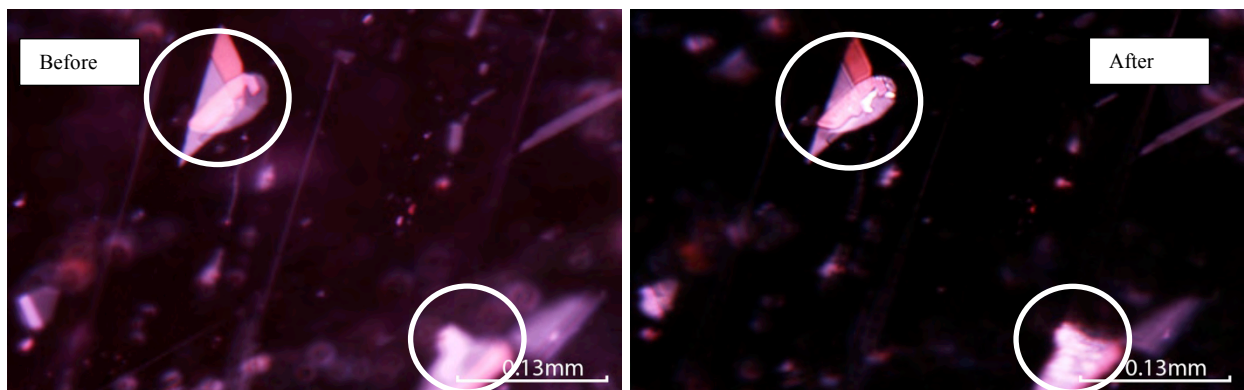


Figure 38: Sample 4073, before (left) and after (right) heat treatment in Bangkok. Before heat treatment we can see highly reflective iridescent platelets and few thin needles. After heat treatment experiment in Bangkok (the stone was heated 3 times at 550°C, 650°C and 750°C) on the main platelet on the left (circled) several bright spots appeared. The same can be seen on the blur platelet on the lower part of the right side of the photo, but sadly it is not clear. Fiber optic light illumination magnified 210x. Photo: V. Raynaud © GIA.

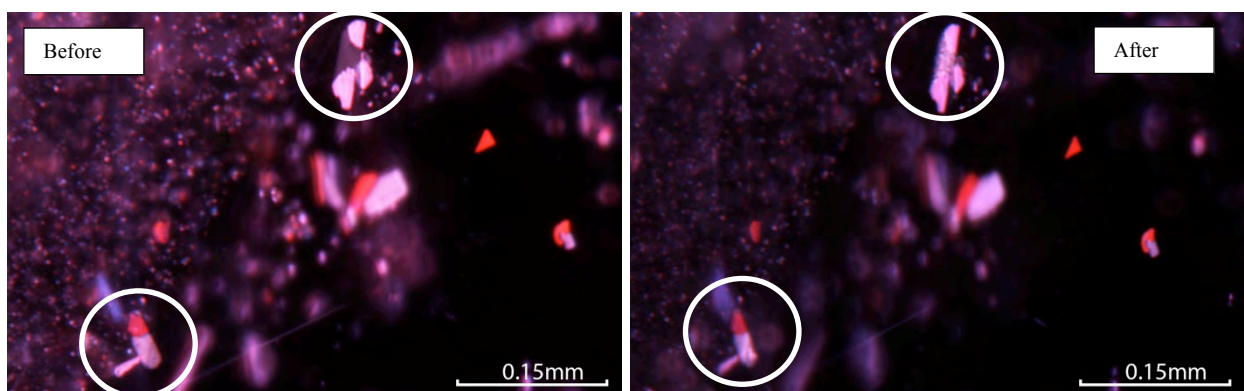


Figure 39: Sample 4059, before (left) and after (right) heat treatment in Bangkok. Before heat treatment we can see highly reflective iridescent platelets and few needles and particles. After heat treatment experiment in Bangkok (the stone was heated 3 times at 550°C, 650°C and 750°C) on the platelet seen in the upper central part of the photo and in the small platelet seen in the lower left area, many spots appeared after heat treatment. Fiber optic light illumination magnified 144x. Photo: V. Raynaud © GIA.

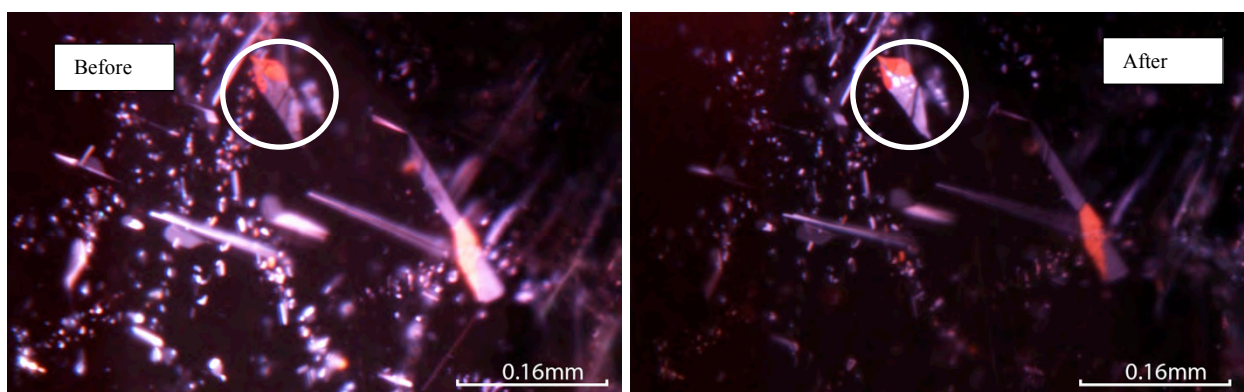


Figure 40: Sample 4059, before (left) and after (right) heat treatment in Bangkok. Before heat treatment we can see highly reflective iridescent platelets and few needles and particles. After heat treatment experiment in Bangkok (the stone was heated 3 times at 550°C, 650°C and 750°C) some bright spots are now well visible on the large platelet on the top of the photo. Fiber optic light illumination magnified 190x. Photo: V. Raynaud © GIA.

In so far as this spottiness, staining or deterioration had thus far not been noted on any platelets present in unheated rubies collected in the field, it may be deemed likely that the presence of these alterations on some platelets is indeed evidence that heat treatment has taken place. However, further experimentation is necessary to test the reliability of these observations.

Infrared Spectroscopy

Infrared spectra were collected from the same area of each sample before and after the primary heat treatment processes carried out in Beruwela. Three interesting features were observed after heat treatment.

Twelve samples showed the 3309 cm^{-1} hydrogen related peak that was present before heating decreased or disappeared after heating in air. For example, the peak height at 3309 cm^{-1} of sample 5320 (heated for greater than one hour in air) was 0.03 cm^{-1} and 0.01 cm^{-1} for before and after heat treatment, respectively (Figure 41). As well as, Sample 5322 (heated for less than one hour in air) (Figure 42) decreased from 0.05 cm^{-1} to 0.01 cm^{-1} after heat treatment.

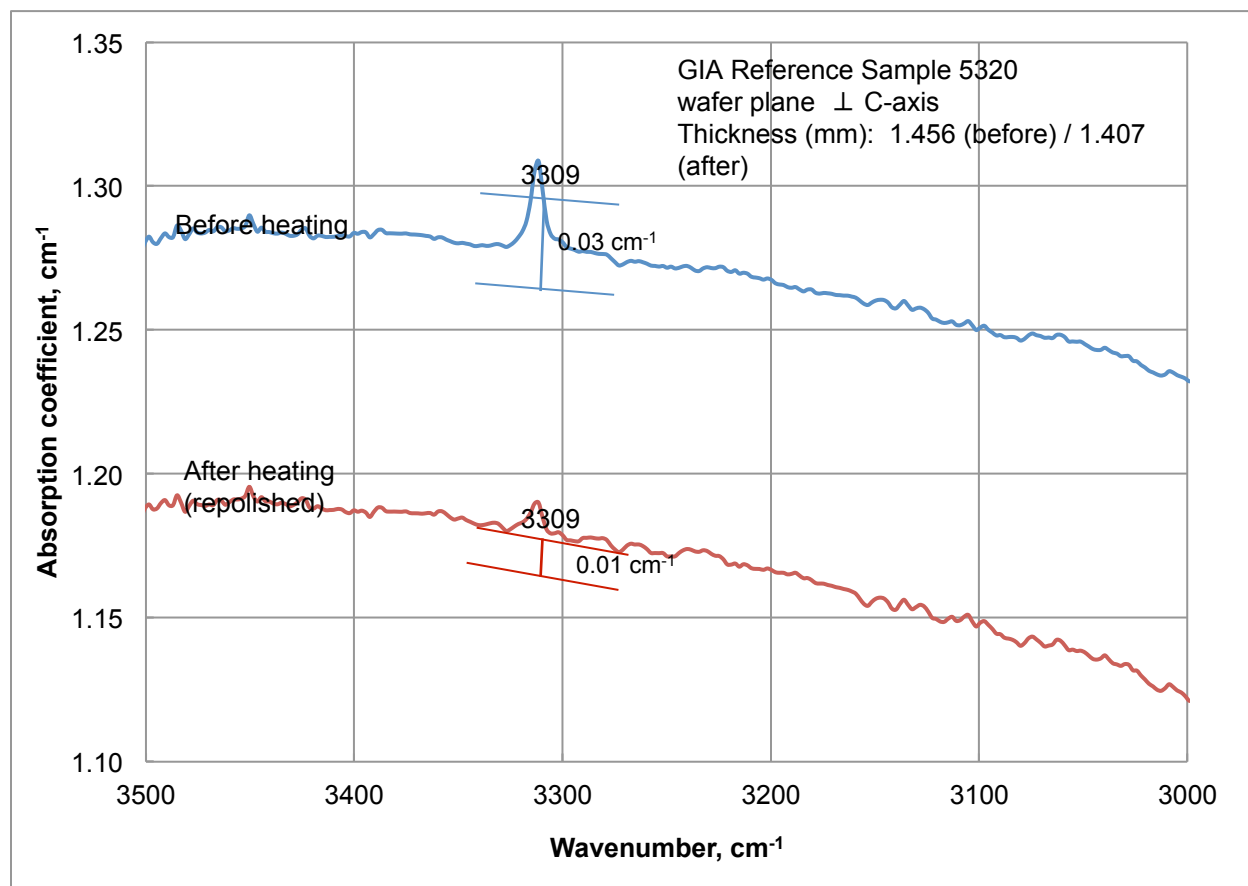


Figure 41: Infrared spectra of sample 5320. Blue and red represent before and after heat treatment, respectively. Optical path length: 1.456 (before)/1.407 (after) mm. Aperture: 1.5×1.5 mm.

Four samples revealed that the 3309 cm^{-1} hydrogen related peak decreased, while peaks at 3232 cm^{-1} and 3186 cm^{-1} were introduced after heat treatment; two samples that were heated in air for “less than one hour” were notable in this respect (Figure 42).

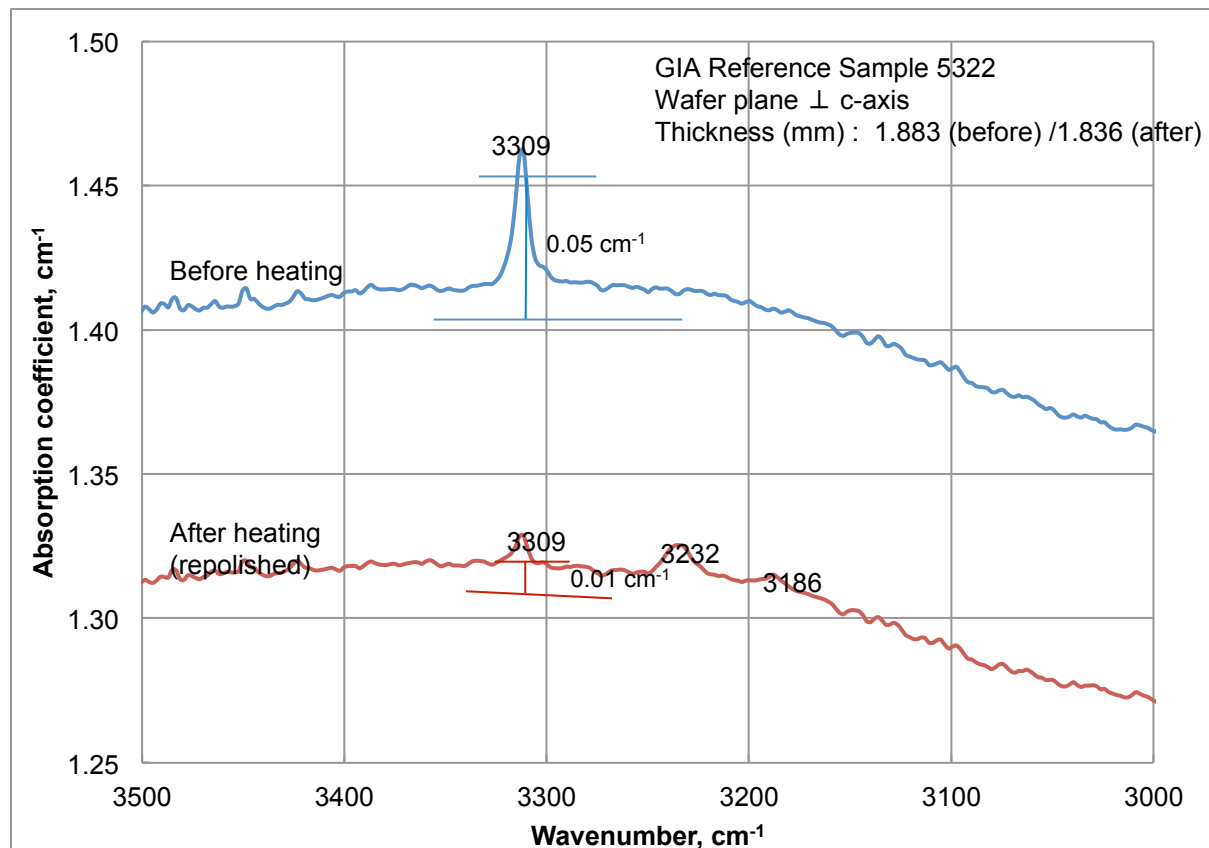


Figure 42: Infrared spectra of sample 5322. Blue and red represent after heat treatment, respectively. Optical path length: 1.883 (before)/1.836 (after) mm. Aperture: 1.5x3.0 mm.

Two samples recorded a peak at 3161 cm^{-1} to which there was insignificant change after heat treatment. The peak height at 3161 cm^{-1} seemed to decrease from 0.067 cm^{-1} to 0.05 cm^{-1} in the spectrum of sample 5327 (heated for “greater than one hour”) when taken through an inclusion free area (Figure 43). However, when an infrared spectrum was recorded through an area containing fine particle inclusions in the same sample (5327), the intensity of the 3161 cm^{-1} increased after heating (Figure 44).

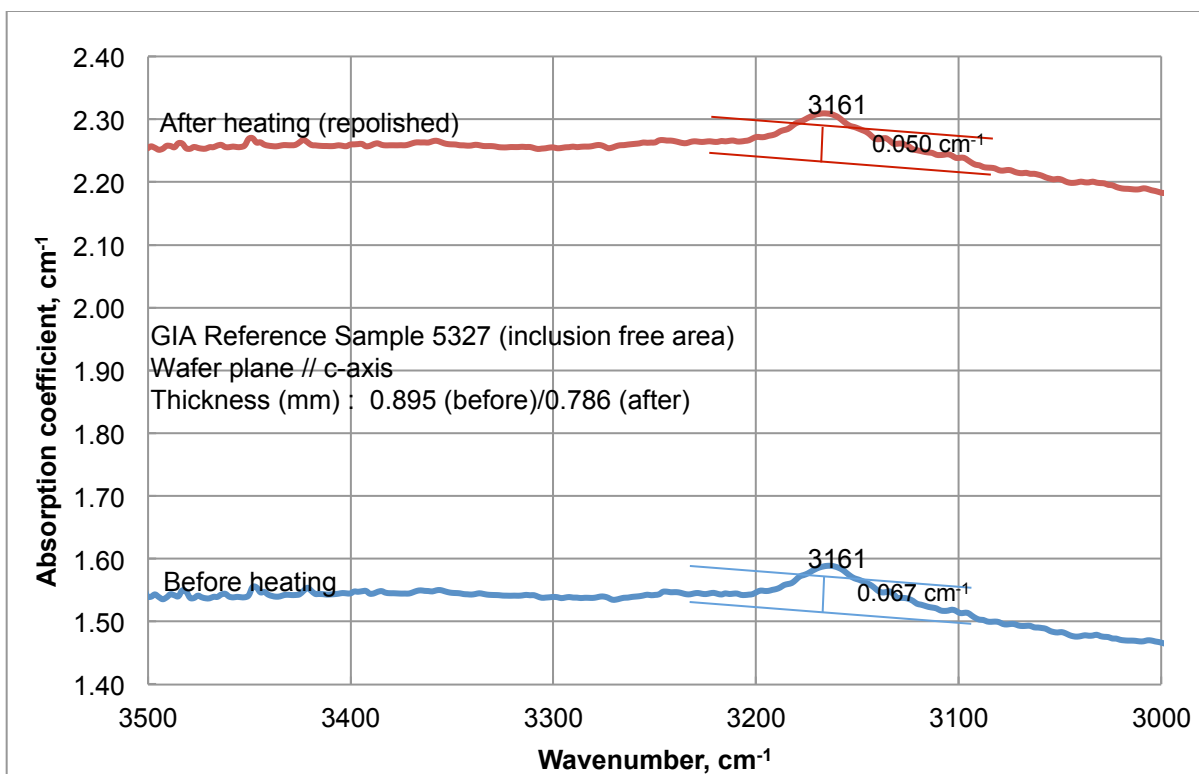


Figure 43: FTIR spectra of sample 5327 taken through an inclusion free area. Blue and red represent before and after heat treatment, respectively. Optical path length: 0.895 (before)/0.786 (after) mm. Aperture: 1.5x3.0 mm.

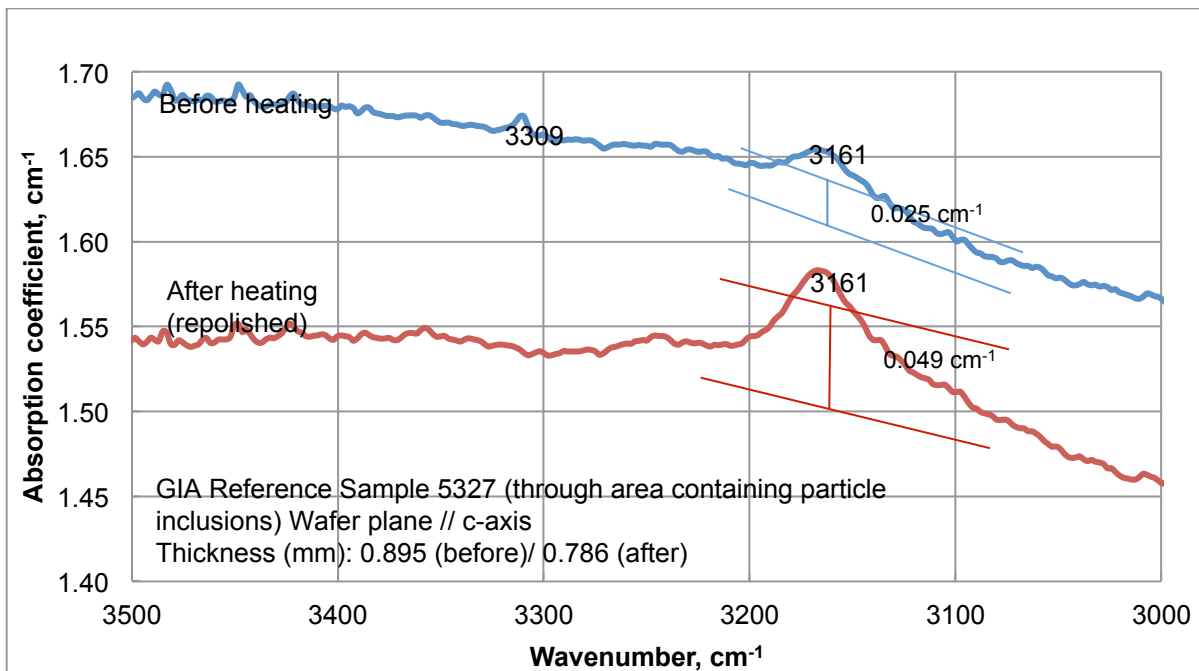


Figure 44: Infrared spectra of sample 5327 taken through an area of fine particle inclusions. Blue and red represent before and after heat treatment, respectively. Optical path length: 0.895 (before)/0.786 (after) mm. Aperture: 1.5x3.0 mm.

Chemistry

Chemical analyses were performed on all wafered samples (see Table 1) both before and after heating in Beruwela. This was primarily carried out to ensure that no external elements were added to the samples during a process for which the authors were not privy to the actual parameters. After heating no additional elements were noted for any of the specimens.

However the chemistry of sample 5327 (Table 6) revealed some interesting data for future evaluation. The inclusion free area the sample contained a higher level of Mg compared with Ti, whereas in the particle rich area the sample contained a higher level of Ti compared with Mg. However, both showed the 3161 cm^{-1} peak with the inclusion free area being the stronger (0.067 compared with 0.025 cm^{-1}). It is interesting to see the strength of the 3161 cm^{-1} increased after heat treatment in the area with particle inclusions present, with no apparent or measurable change in chemistry.

Table 6: LA-ICP-MS results for GIA reference sample 5327 before and after heated in inclusion free and particles areas.

Sample 5327		concentration in ppma (average \pm SD)					
		^{24}Mg	^{47}Ti	^{51}V	^{52}Cr	^{56}Fe	^{69}Ga
Inclusion free	Before heated	72 ± 4	36 ± 3	4 ± 0.3	867 ± 50	1596 ± 85	9 ± 1.0
	After heated (repolished)	73 ± 2	40 ± 2	4 ± 0.2	942 ± 36	1503 ± 44	9 ± 0.6
Particles	Before heated	23 ± 1	45 ± 19	4 ± 0.4	1024 ± 102	1644 ± 33	10 ± 0.4
	After heated (repolished)	24 ± 1	40 ± 23	4 ± 0.3	977 ± 61	1493 ± 70	10 ± 0.3

Summary:

Inclusions:

A microscopic examination of inclusions seems to be a useful tool for gemologist wishing to find out if a given ruby from Mozambique is or is not heated at “low temperature”. It is advisable to use a high magnification microscope in conjunction with fiber optic lighting.

- In many cases heat treatment had consequences for mineral inclusions as discoids and fractures appear around crystals. Usually the larger crystals are affected first. Not all mineral inclusions are affected the in the same manner: Mica, feldspar and chalcopryite crystals are more likely to be affected by this treatment than amphibole crystals.
- Fractures (with limonite / iron stains) can also show some differences (darkening of the iron stain: bright orange before heat, darker after heat)
- In the case of the wafers no significant changes in the aspect of needles and particles were noted.
- In the case of the secondary heating experiment (three faceted stones heated in Bangkok), the surface of some of the platelets was observed to have altered. Some spottiness, staining or deterioration similar to that seen in commercially heated stones from the reference collection was observed.

FTIR spectroscopy

Three interesting features were observed after heat treatment in air:

- A peak at 3309 cm^{-1} decreased or disappeared
- A peak at 3309 cm^{-1} decreased and peaks at 3232 and 3186 cm^{-1} introduced
- A peak at 3161 cm^{-1} decreased (slightly) in an inclusion free area.
- A peak at 3161 cm^{-1} increased (slightly) in an area containing fine particle inclusions.

LA-ICP-MS

- Limited trace elements found in ruby from Montepuez e.g., Mg, Ti, V, Cr, Fe, and Ga
- There was no significant changed in chemical analysis between before and after heat treatment. This can imply that there was no external chemical applied in low heat treatment process in this study.

Special Thanks:

To Mr. Fowsan, Mr. Ashkar Ali Mubarak, Mr. Armil Sammoon and Mr. Punsiri Tennakoon to have helped us to do this experiment in Beruwala.

To Dr. Laurent Massi and Karim Guerchouche for their support for the heat experiment in Bangkok.

To the team at the GIA Laboratory Bangkok for their support and finally last, but not the least to Shane McClure, Ken Scarratt and Dr. John Emmett for their useful advice, time and support.

Annex A: GIA Field Gemology cataloguing System

This system was developed at the GIA Field Gemology department to precisely document the way in which a given research sample was collected.

A conditions: Mined/collected by the field-gemologist.

A1: Collected in-situ from a primary deposit by the field-gemologist.

A2: Collected on the floor/mine waste at the mine (primary/secondary) by the field-gemologist.

A3: Collected after digging in a secondary deposit by the field-gemologist.

B conditions: Field-gemologist witnessed the mining.

B1: Collected on site in jig/sieve from the mine in a secondary type deposit by field-gemologist.

B2: Collected on site in miner's bottle from mine in a secondary type deposit by mines or by field-gemologist.

C conditions: Field-gemologist collected from miners at the mine but without witnessing the mining process.

C1: Collected at mine from mine owner (not mined that day in front of field-gemologist's eyes).

C2: Collected at mine from miner on site (not mined that day in front of field-gemologist's eyes).

D conditions: Field-gemologist collected the stones from miner but not at the mines.

D1: Collected from mine owner (at HQ near the mines).

D2: Collected from miner (near the mines).

D3: Collected from person claiming to be a miner (mine not visited).

D4: Collected from miner in regional/international market.

E conditions: Field-gemologist collected the stones from a secondary source close to the mines.

E1: Bought from trusted secondary source (gemologist/dealer/broker) at local market (close to source).

E2: Bought from trusted secondary source (gemologist/dealer/broker) at regional market (close to source).

E3: Bought from unknown secondary source at local gem market (close to source).

E4: Bought from unknown secondary source at regional gem market (close to source).

F conditions: Field-gemologist collected the stones from a secondary source in international market.

F1: Bought from unknown dealer at international gem market (gem show...).

F2: Bought from trusted source (gemologist/collector/dealer...) in an international market.

F3: Bought from a lab client after the stone was submitted to the GIA Laboratory.

Z conditions: No information about how the stone was collected.

Z1: Lost information.

Z2: No information.

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