

Sapphire Heated with Pressure

By members of the LMHC:

- CGL Central Gem Lab, Japan
- CISGEM, Italy
- DSEF German Gem Lab, Idar-Oberstein, Germany
- GIA Gemmological Institute of America
- GIT Gem and Jewelry Institute of Thailand
- Gübelin Gem Lab, Switzerland
- SSEF Swiss Gemmological Institute, Switzerland



Plus...

- Lotus Gemology, Thailand
- ICA Lab, Thailand
- Dunaigre Consulting, Switzerland
- GJEPC-GTL, India
- Hanmi Lab, Korea

Questions regarding pressure heated sapphire

- Increased supply of sapphires on the market?
- Inclusion damages?
- Fissure healing?
- Addition of foreign elements?
- Durability / stability issues?

Historic context:



circa 1045 AD

First account (Al-Biruni) of heat treatment of rubies/sapphires at temperatures up to 1100°C using a blowpipe, e.g. to remove the blue tint from rubies.

20th century



1916

Heated basaltic sapphires from Ethiopia.

Heat treatment of dark blue (basaltic) sapphires from Queensland (Australia) to lighten their color. This process is later adapted for heating all dark blue basaltic sapphires and continues to this day. It is difficult to detect as these stones have already experienced a natural heating within the basaltic magma during their uplift to the Earth surface.

20th into 21st Century:

Two different tracks of heat treatments



Heating **with no** diffusion of colouring elements from external source and **with no** addition of a flux to fill or even “heal” fissures



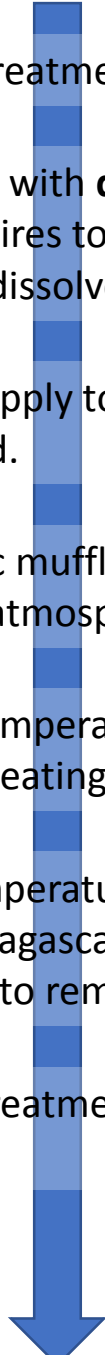
all variations of heating methods are commonly summarised and disclosed only as **heated**



Heating **with** diffusion of colouring elements from external source to produce colour and/or assisted **with** a flux to fill or even “heal” fissures



Each different method is **specifically disclosed.**



Before 1960: Heat treatment using **basic equipment** (e.g. blow pipe)

1966–1980: Heating with **diesel furnaces** (1500°C) to convert Sri Lankan geuda sapphires to blue (hydrogen diffusion in reducing conditions!). Rutile dissolves resulting in enhanced clarity.

1979: Oxygen gas supply to furnace results in higher temperature and thus better yield.

Early 1980's: Electric muffle furnaces are introduced, allowing much better control over atmosphere and temperature.

About 1983: High temperature “Toda” furnace is introduced, thereby improving heating results.

Early 2000: Low temperature-heating of corundum (e.g. pink sapphires from Madagascar and rubies from Mozambique) at oxidizing conditions to remove blue tints.

2004: Punsiri heat treatment producing sapphires with a colourless rim.

Heating **with no** diffusion of colouring elements from external source and **with no** addition of a flux to fill or even “heal” fissures

all variations of heating methods are commonly summarised and disclosed only as **heated**

Heating **with diffusion** of colouring elements from external source to produce colour and/or assisted **with a flux** to fill or even “heal” fissures

Each different method is **specifically disclosed**.

1980: Titanium-diffused sapphire (Ti *from external source*) enter the market. Colour only very shallow and surface related. Specifically disclosed !

Mid-1980's: Additions of flux during heating to assist fissure healing, resulting in distinct clarity enhancement (e.g. Mong Hsu rubies). Glassy residues remain in healed fissures. Specifically disclosed !

Since Mid-1990's: Beryllium diffused corundum slowly infiltrate the market. In 2001 the market is flooded with Be-diffusion treated sapphires of padparadscha-like colour. Specifically disclosed !

2003: Beryllium diffusion applied on blue sapphires to lighten the color. Specifically disclosed !

2004: Corundum with lead glass filled fissures enters the market. Specifically disclosed !

2012: Corundum with cobalt-doped lead glass in fissures to produce a vivid blue colour enters the market. Specifically disclosed !

Since 2009: Blue sapphires heated with pressure enter the market

How to disclose them ?



Series of sapphires heated with pressure

Heating with Pressure Treatment Methodology

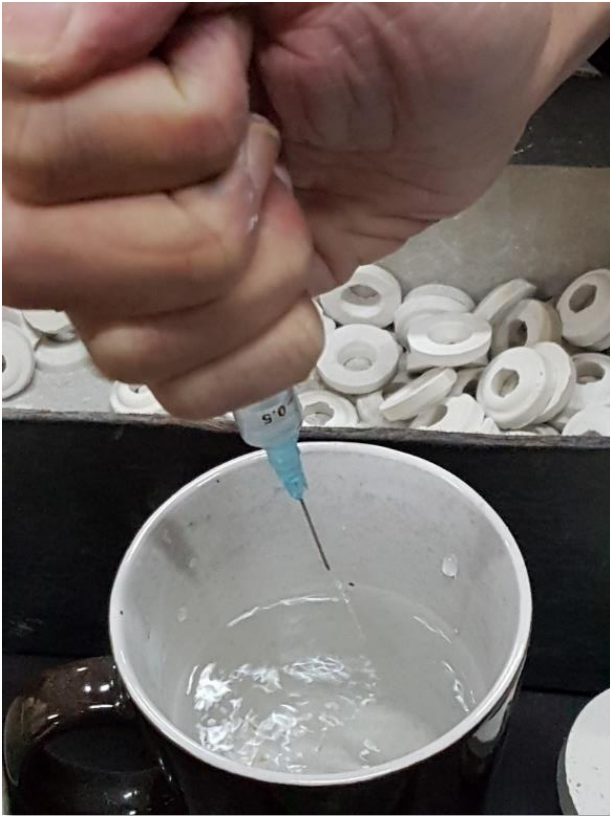
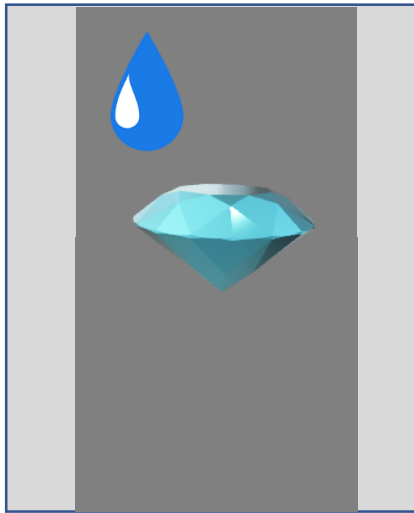
Following information is based on visits to the heating facility in South Korea by Hanmi Lab, GIT Thailand, and GIA.

Sample Preparation



Graphite is packed around the sapphire in the crucible (reducing conditions !)

Option to add some water



Commonly few drops of water are added into the graphite filled crucible.

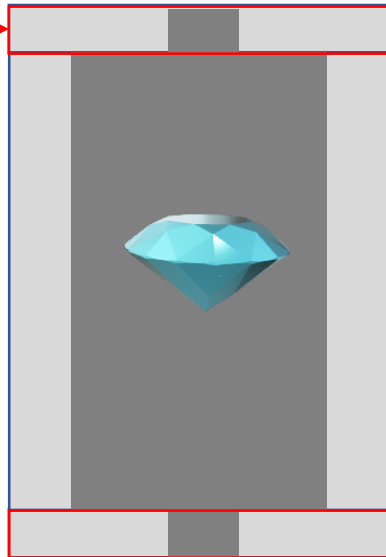
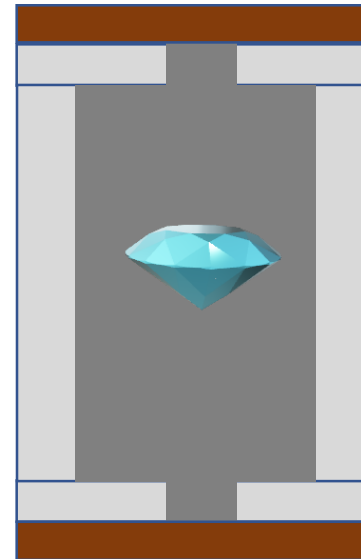
Closing and sealing of crucible



crucible
cover



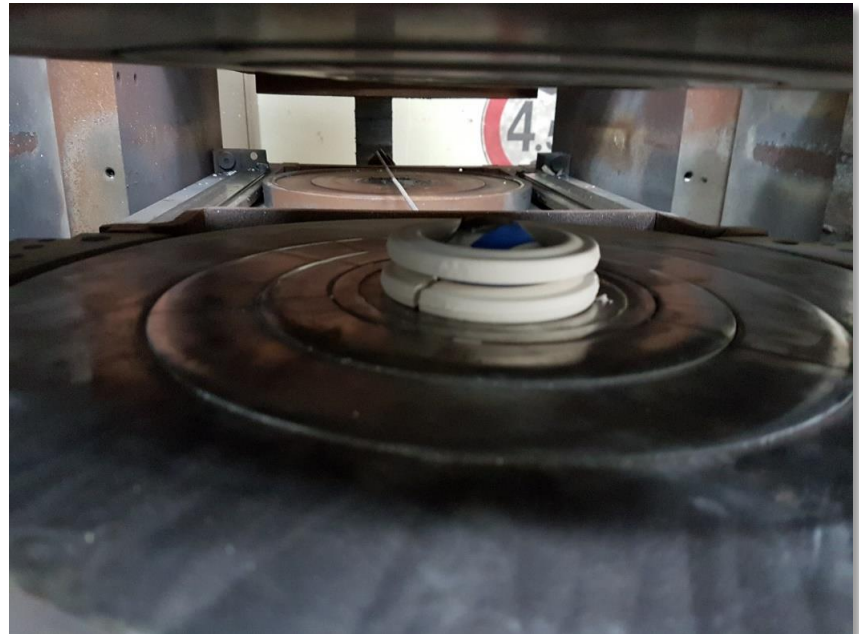
metal (Mo)
plate



Furnace used for treatment



Mold Press Machine



Mold press machine & controller

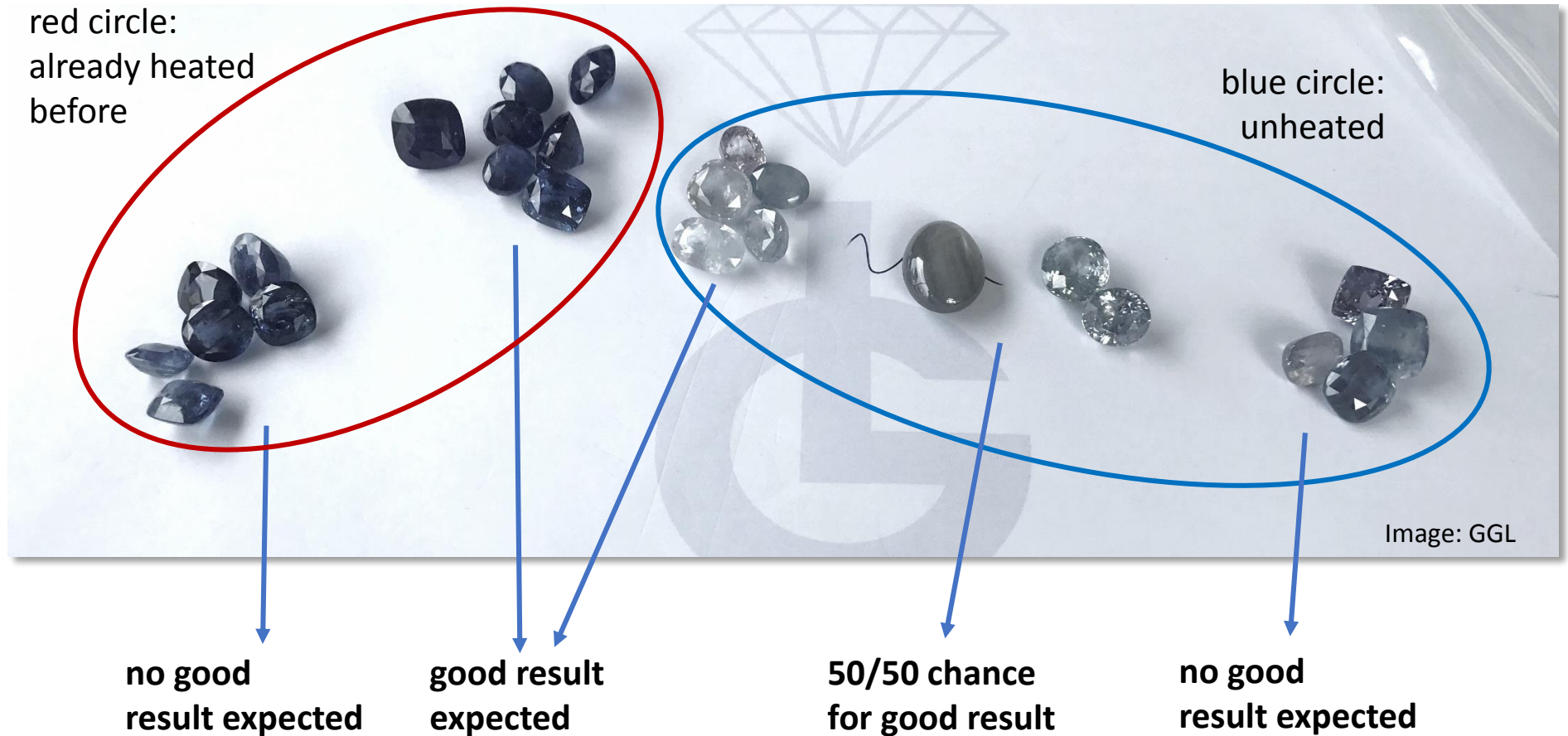
Images: GIT

Starting material used for treatment



Parcel of sapphires for
treatment at the factory.
Photo: Shane McClure, GIA

Starting material used for treatment



Expected results after treatment based on experience of Sri Lankan dealer

Results of treatment



Examples of samples before and after heating with pressure

Not all stones result in better colours



From Choi et al. 2018, Photos by Photo by P. Ounorn

Left: before, right: after treatment: variability of resulting colours, with some stones with no colour change or even lighter colour after the treatment.



Original trace element concentration in each individual stone greatly influences the result.

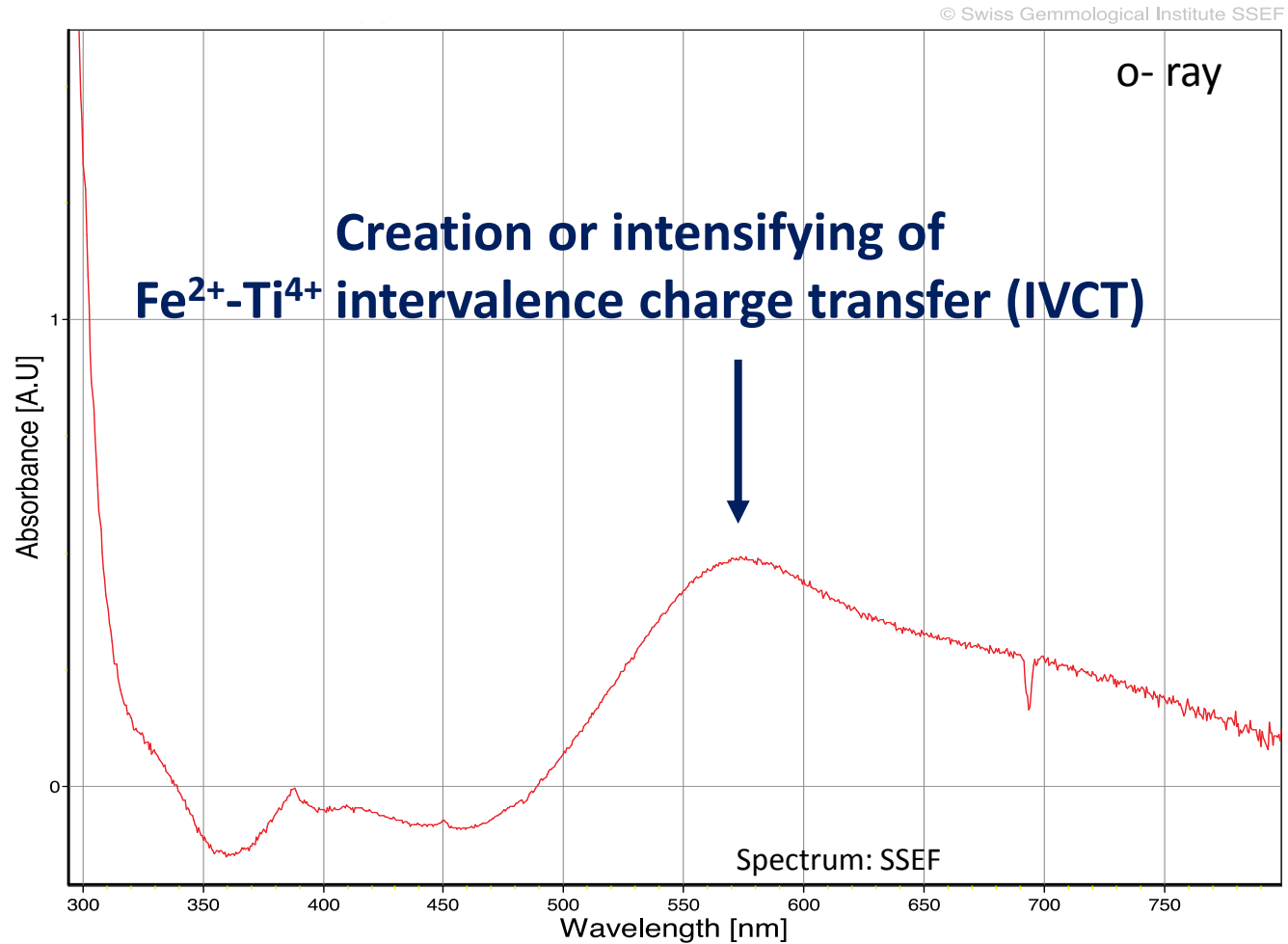
Repolishing required



Photos:
Imam Gems

As a result of the treatment in the graphite crucible, the sapphires have to be repolished after treatment to get rid of the carbon layer.

Cause of colour improvement



This IVCT absorption band is the common cause of blue colour in most sapphires (unheated and heated!)

No diffusion of colouring elements !

Sample	Li	Be	Mg	Ti	V	Cr	Fe	Ga
SAXX064	<0.09	1.0	80	110	7	4.5	530	120
SAXX065	0.25	0.8	100	200	11.5	2.7	1700	165
SAXX066	0.18	0.34	115	290	55	8	550	95
SAXX067	<0.1	<0.22	<0.6	34	1.4	2.0	2200	260
SAXX068	<0.1	0.19	120	220	7.5	22	480	61
SAXX069	<0.09	<0.18	45	120	8	3.8	350	69
SAXX070	<0.08	<0.16	50	150	8.1	6.5	380	75
SAXX071	<0.09	<0.2	62	95	9.5	6.8	550	83
SAXX072	<0.09	<0.17	77.5	120	12.7	6.0	590	60
SAXX073	<0.09	0.23	240	330	25	2.3	150	87
SAXX074	<0.15	<0.5	240	700	18	8	1150	135
SAXX075	<0.09	0.25	160	270	28.2	3	480	66

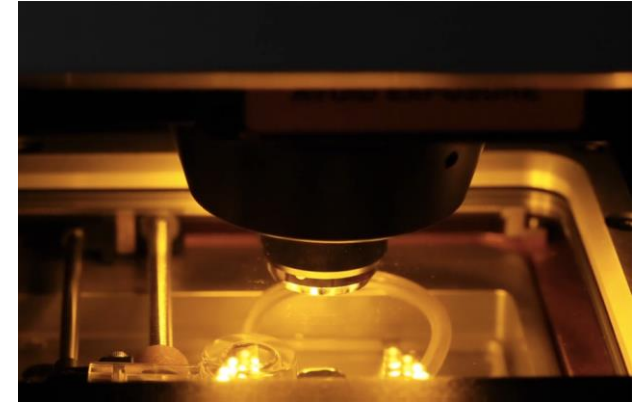


Photo SSEF

LA-ICP-MS tests on 12 samples from GGL gave the following results (average of 3 laser spots per sample; in ppm).

Specifically, no diffusion of beryllium, lithium, or titanium.

Heating with Pressure Inclusion Study

Comparison of specific features before and after heating with pressure

Before



After

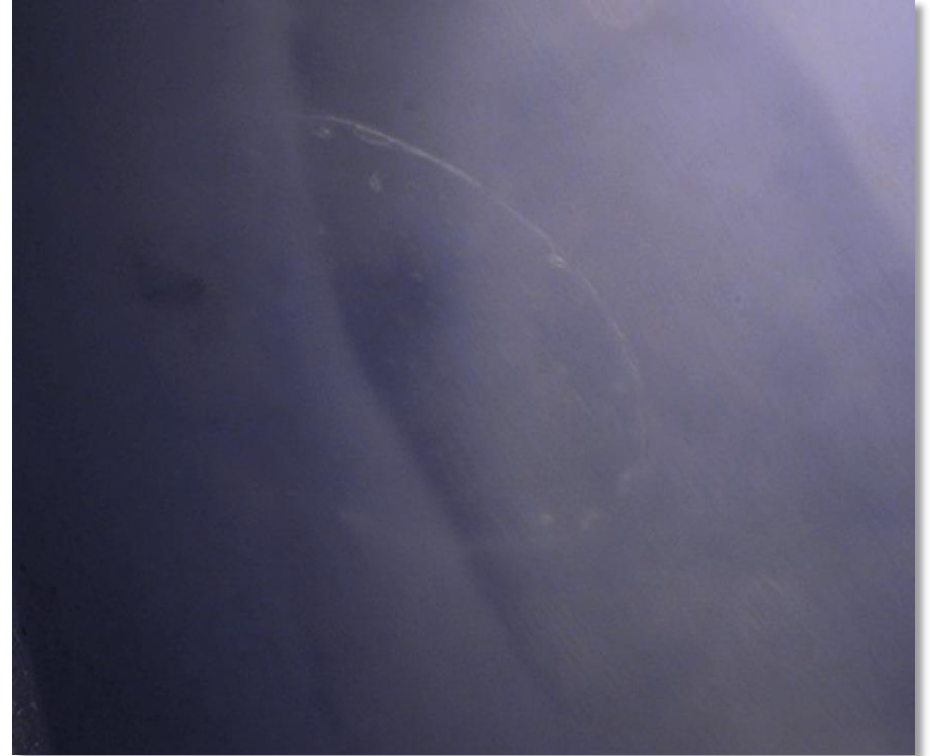


After heating with pressure: Serious deterioration of clarity with new fissures resulting from the treatment.

Before

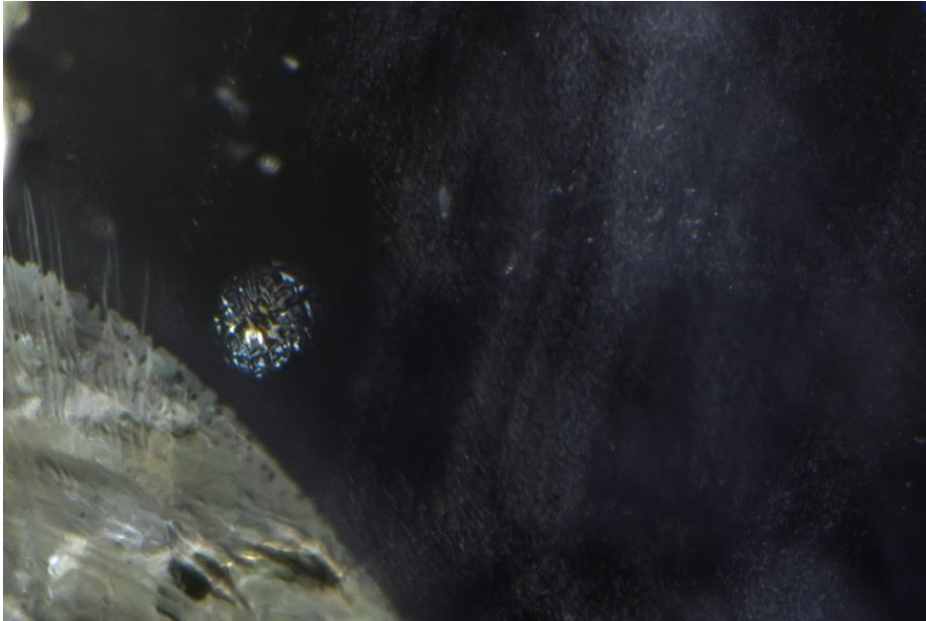


After



After heating with pressure: Improvement in clarity due to the healing of a narrow-gap fissure.

Before

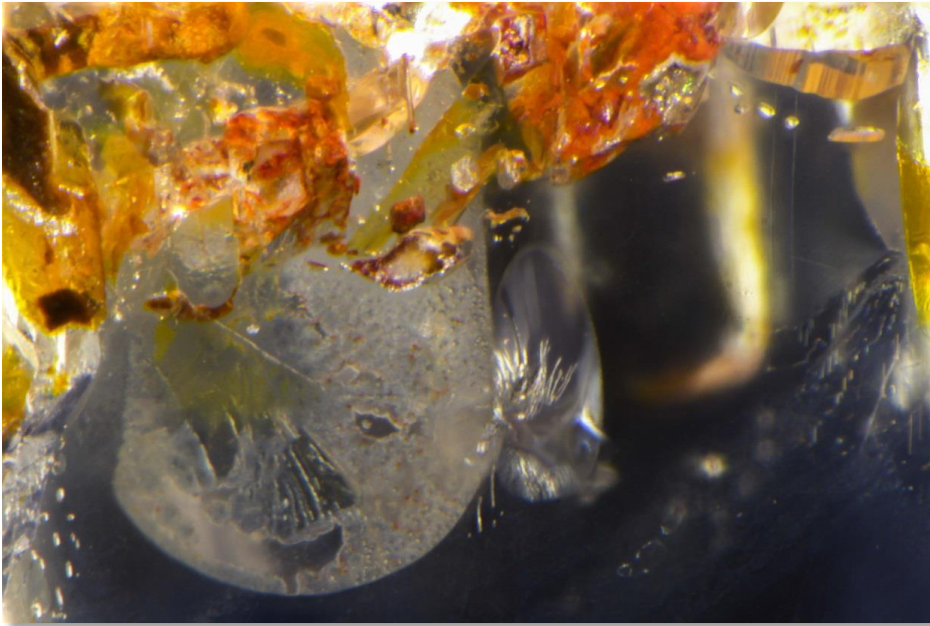


After

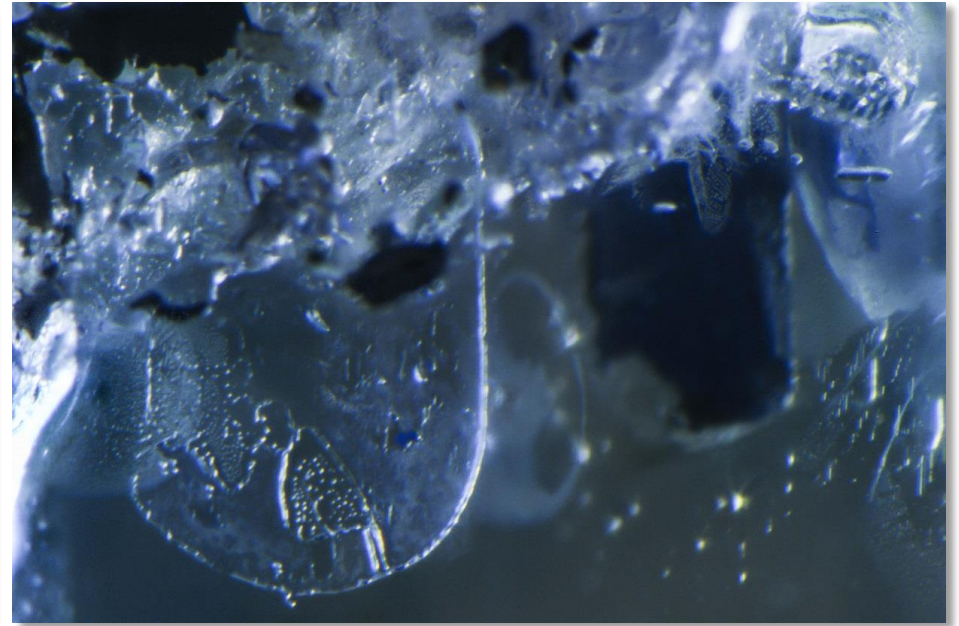


After heating with pressure: Improvement in clarity due to the healing of the narrow-gap fissure at lower left and the halo around the crystal inclusion.

Before

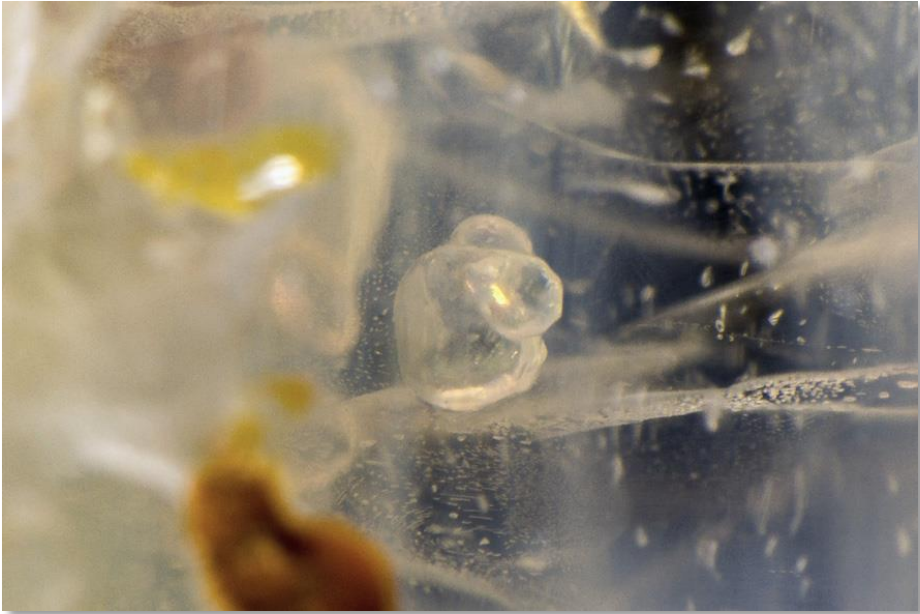


After

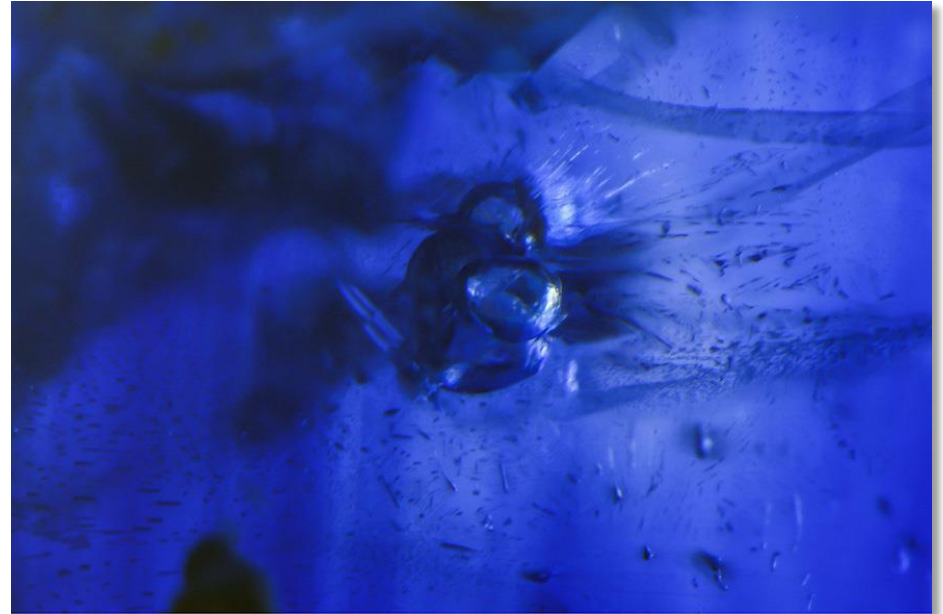


After heating with pressure: Iron staining gone, fissure in the middle partially healed but still quite visible.

Before



After



After heating with pressure: Typical damage from high temperature heat treatment, also a great improvement of colour.

Heating with Pressure Durability Study

For this study, samples were chosen from three categories:
a) eye clean, b) included, c) heavily included

In addition, one sample was faceted after treatment.

1) Ultrasonic Cleaning

Testing time	Category A	Category B	Category C
Before	 3 mm	 3 mm	 3 mm
5 minutes	 3 mm	 3 mm	 3 mm
10 minutes	 3 mm	 3 mm	 3 mm
30 minutes	 3 mm	 3 mm	 3 mm

The ultrasonic bath was filled with slightly warm water. All samples were placed on a wire bucket and soaked in ultrasonic for 5, 10, and 30 minutes respectively. The test at GIT revealed **no damage** on any of the stones.

A similar setup was chosen at GGL for four sapphires revealing by microscopic inspection no additional damage on top of the pre-existent abrasions after the ultrasonic bath.

2) Resistance to Acids

Acid solution	Category A	Category B	Category C
Before			
HNO ₃			
HF			

Three sapphire samples (one of each category) were selected for:

- a) soaking in strong nitric acid (HNO₃) for six hours and
- b) strong hydrofluoric acid (70% HF) for two minutes.

No etching whatsoever occurred.

3) Testing of Brittleness (Paper Clip/Steel Blade)



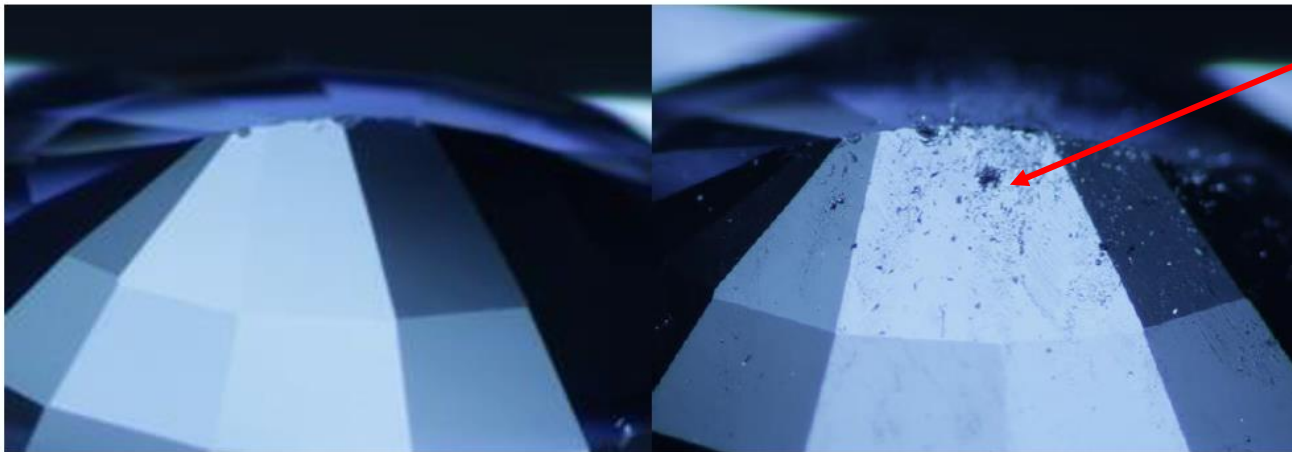
(A)



(B)

Three stones (one of each category) were selected to be scratched by a paper clip (A) and cutter blade (B).

We observed no damage to the stones, only flakes of metal that came off the paper clip and accumulating on the surface.



4) Durability (Drop Testing)

Three stones (one of each category) were selected and dropped onto a hard concrete floor from approximately one meter height.

This procedure was repeated three times for each stone.

No damage (cracking) was observed in any of the samples.

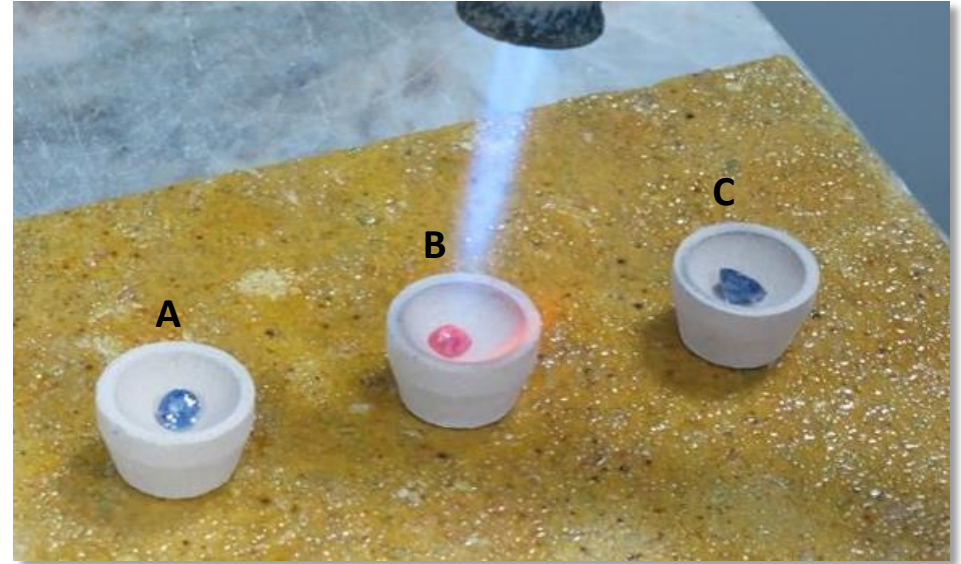


5) Resistance against Thermal Shock

Three stones (one of each category) were selected and heated with a jewellery torch burner for five seconds until each of them started to glow red.

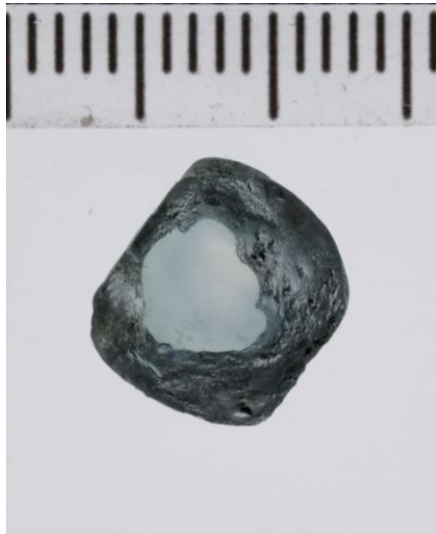
No change of color occurred due to the testing.

One stone from category C (highly included!) developed tension cracks extending from internal inclusions.

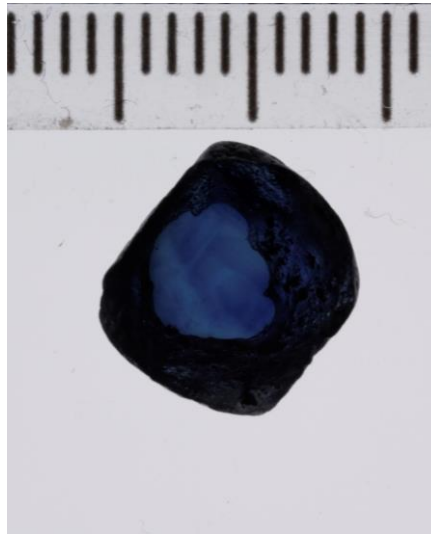


Order	Category A	Category B	Category C
Before			
After			

6) Repolishing



Before – 4.68 ct



After – 4.68 ct



Cut – 1.86 ct

This Montana sapphire from the GIA reference collection was heated with pressure in Korea and subsequently faceted. No damage occurred during polishing and cutting.

Key results from durability study

- No damage when exposed to ultrasonic bath
- No alteration when exposed to acids
- No damage when tested with paperclip or knife blade
- No damage when dropped to the ground
- No color alteration when exposed to jeweler's torch (but one heavily included specimen did develop fissures)
- No unusual behavior when cutting the gems after treatment, confirmed independently by several experienced gem cutters.

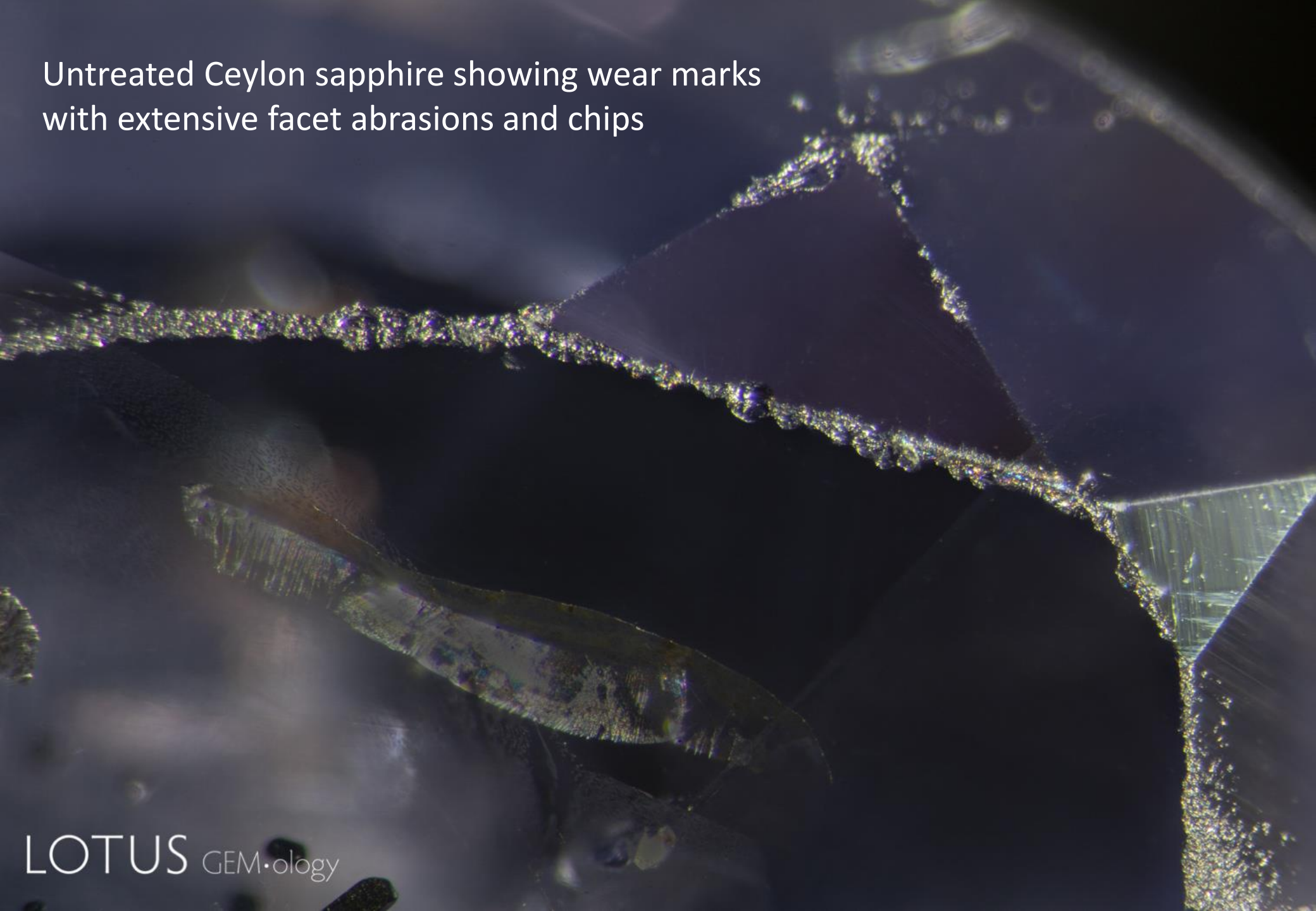
Key results from durability study

- The claim of specific brittleness of sapphires heated with pressure could not be substantiated by our tests, which were carried out by several laboratories simultaneously.
- But indeed: Heavily included starting material (low quality) may produce fissures and cracks (durability issue) regardless of which heating method („traditional“ or „new“) is applied.



Image: SSEF

Untreated Ceylon sapphire showing wear marks
with extensive facet abrasions and chips



A lesson from the past



“ Despite their hardness, ruby and sapphire need to be handled with some care, for they are to a slight extent brittle and if dropped on a hard surface or given a sharp blow tend to develop internal flaws and cracks.

Robert Webster, Gems 1962

Heating with Pressure Treatment Detection

Microscopic Observations

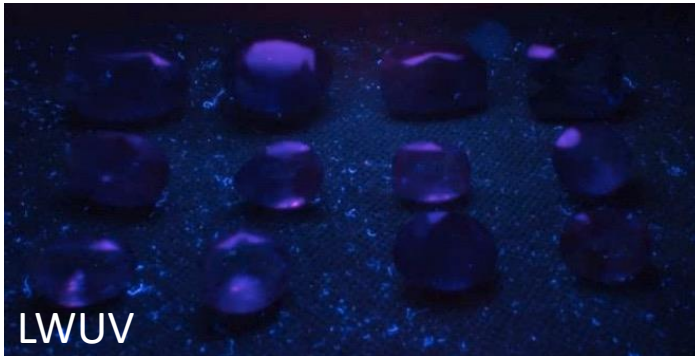
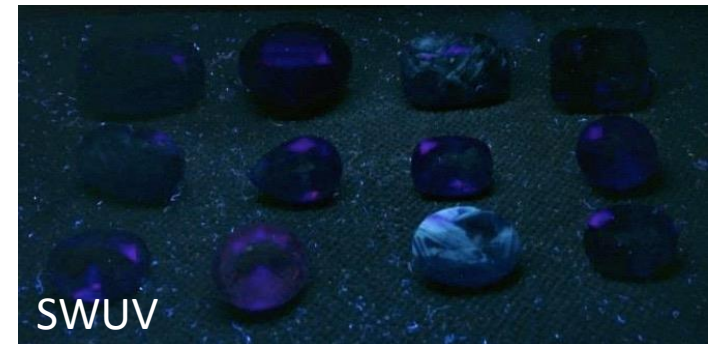
- Mostly similar features as in “traditionally” heated sapphires
- Subtle differences in surface granularity of healed fissures. But somewhat similar features can also be seen in conventionally heated sapphires.
- Sometimes graphite accumulations in fissures and cavities close to the surface (from the graphite filled crucible!)



In most cases **no** evident microscopic feature to detect this treatment apart from common heating features.

UV reaction

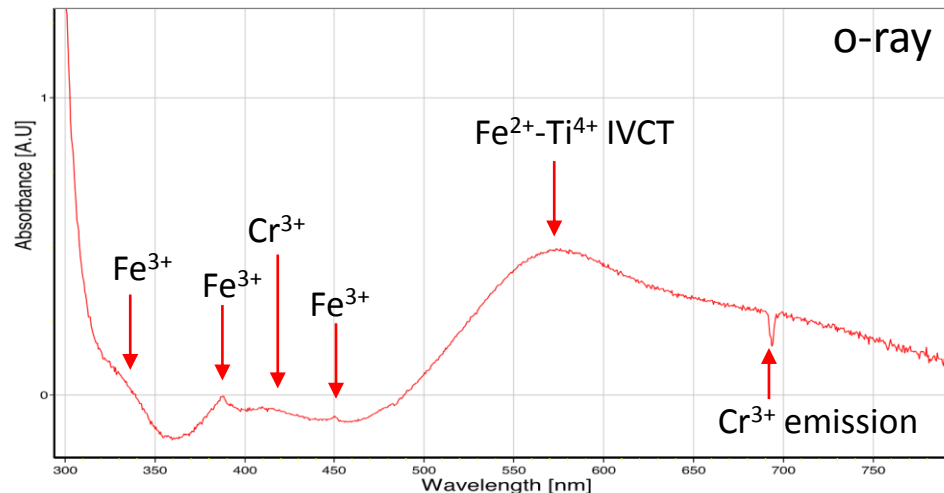
- Very similar to “traditionally” heated sapphires
- Partly no reaction under long and short wave ultraviolet
- Partly chalky white zones at surface under short wave ultraviolet



→ **No** specific ultraviolet reaction which would enable to detect this treatment.

UV-Vis absorption spectroscopy

- Very similar to any sapphire, whether heated or unheated
- Absorption spectrum dominated by $\text{Fe}^{2+}\text{-Ti}^{4+}$ IVCT absorption band, optionally with additional absorption peaks by Fe^{3+} and Cr^{3+}



→ **No** specific absorption feature to detect this treatment.

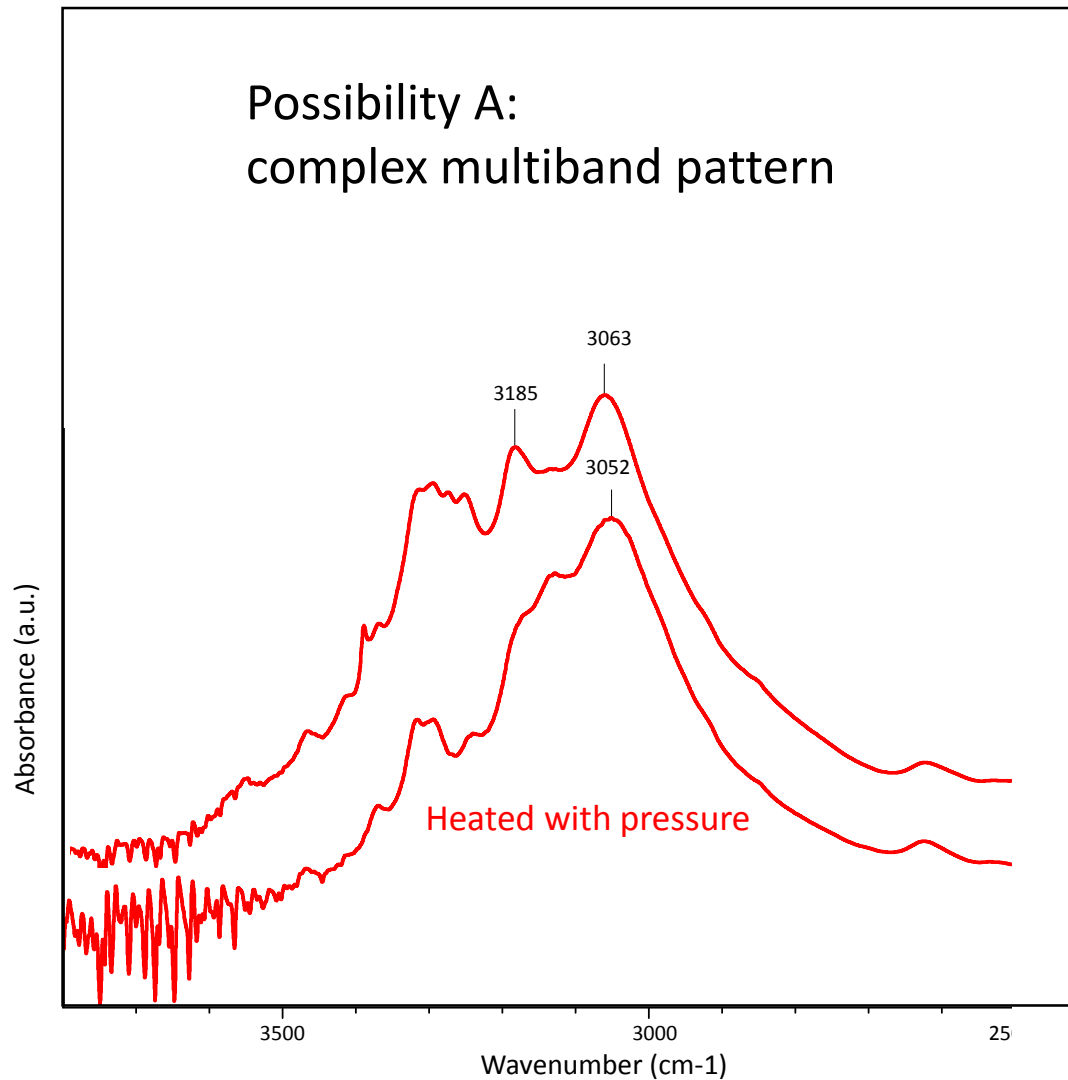
Trace element composition (ED-XRF, LA-ICP-MS)

- No diffusion of beryllium, lithium, titanium from an external source
- The trace element composition is similar to other sapphires, whether heated or unheated and rather linked to their formation and origin (geological setting).
- Residues of the crucible filling are removed after treatment from the surface by the repolishing and thus not accessible anymore to chemical testing.

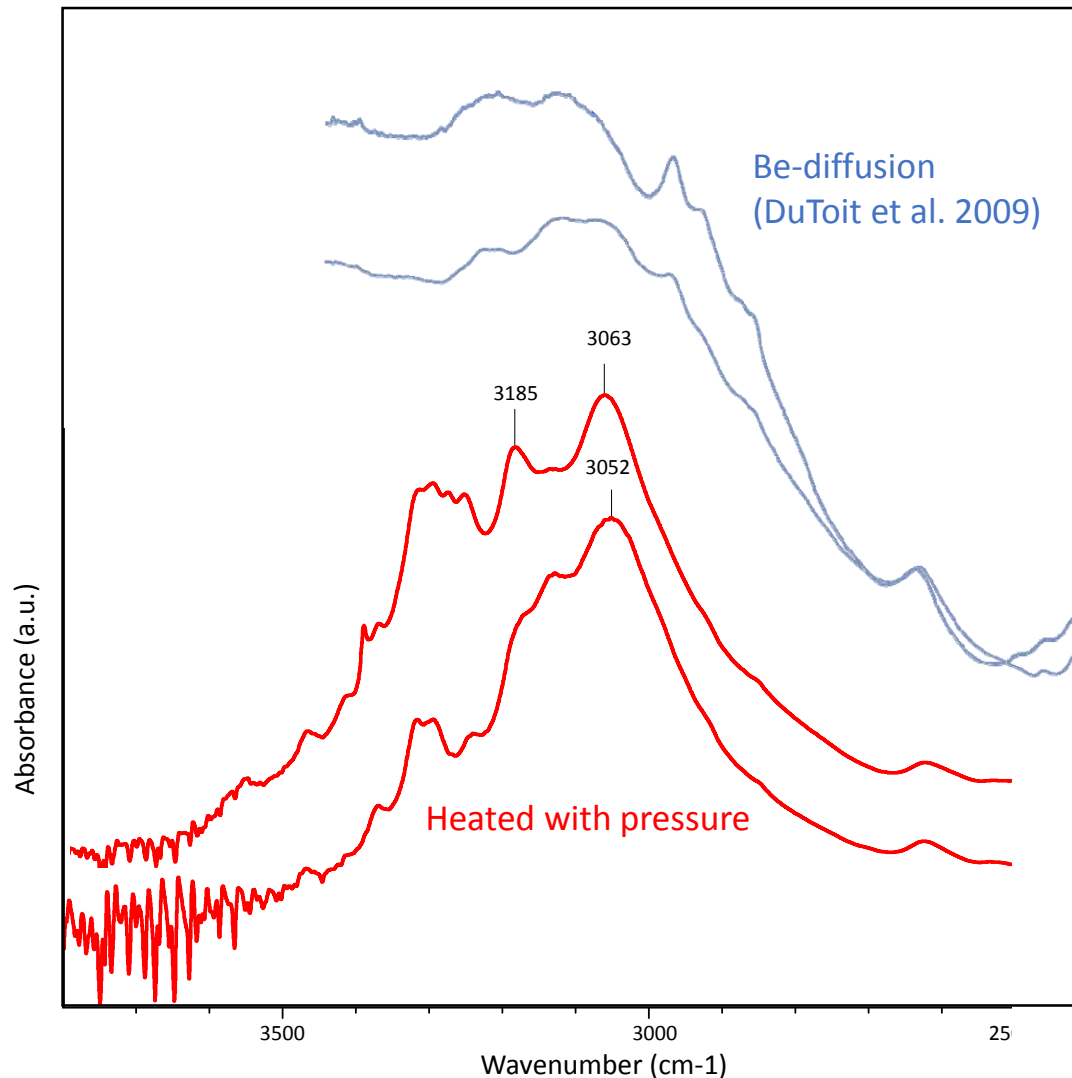
→ **No** specific trace element to detect this treatment.

Heating with Pressure IR Spectra

IR Spectra of Sapphires heated with Pressure



IR Spectra of Sapphires heated with Pressure



Punsiri-heated sapphire

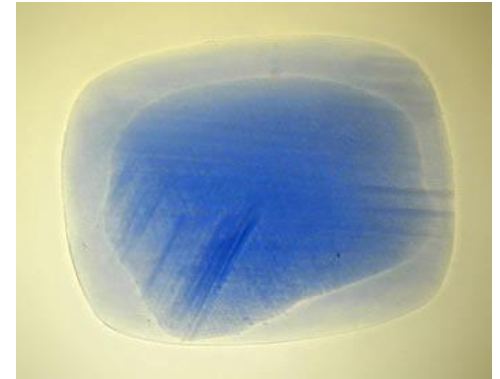
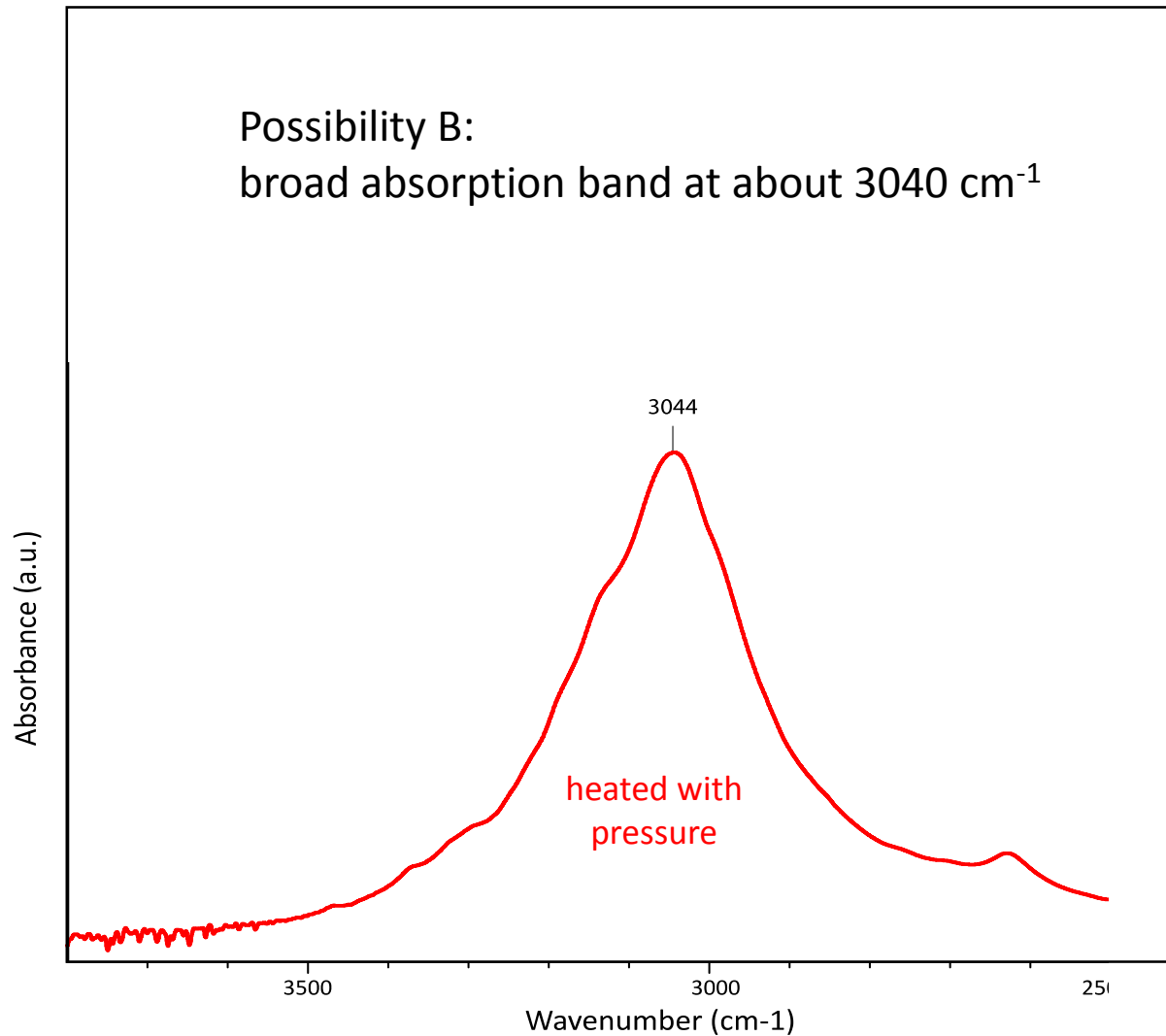


Image: R. Hughes

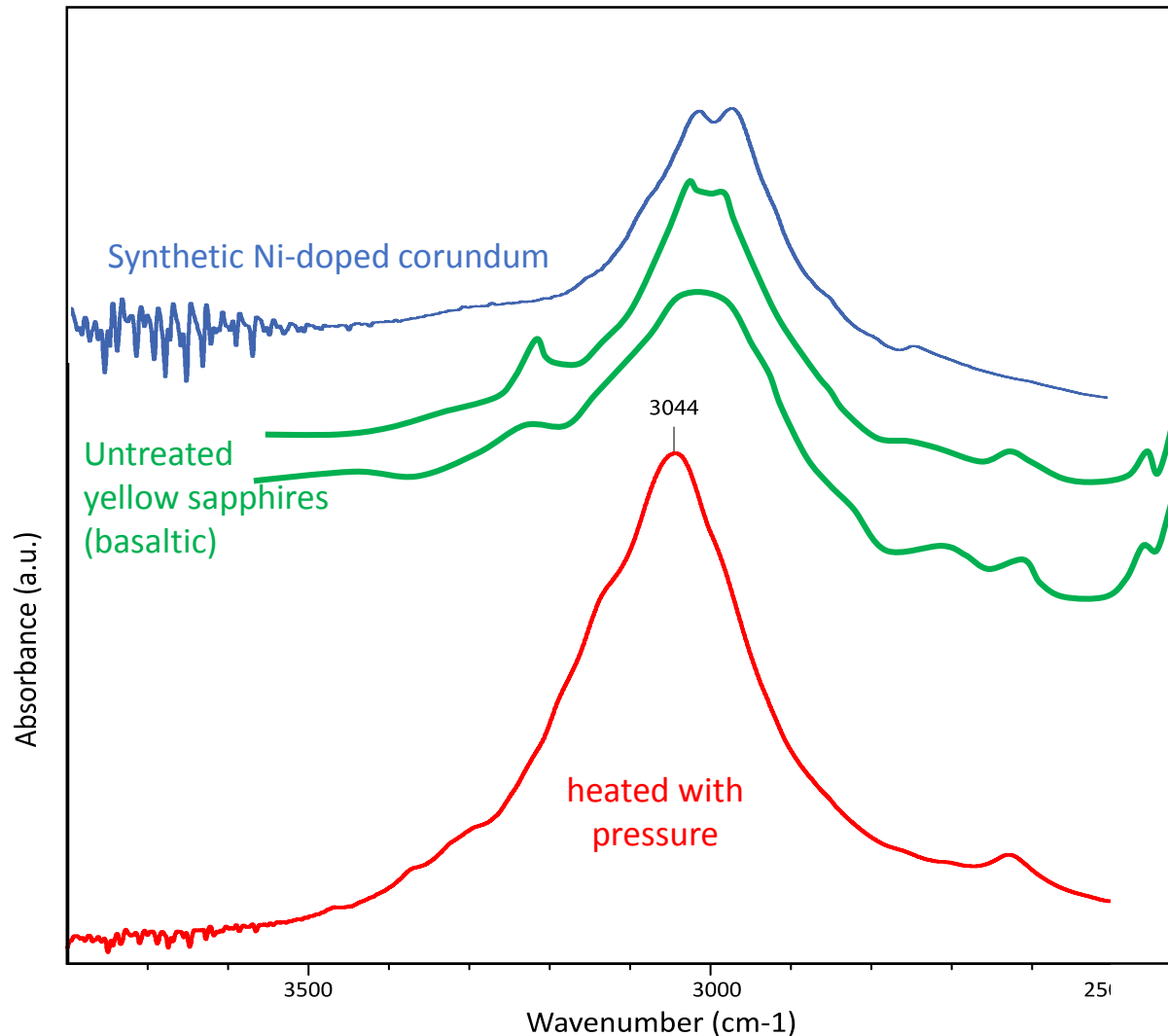
Similar complex “Punsiri-type” pattern have been reported from Punsiri-heated sapphires (disclosed only as heated by the trade) and Be-diffusion treated sapphires. See also DuToit et al. 2009. and Hughes 2017.

IR Spectra of Sapphires heated with Pressure



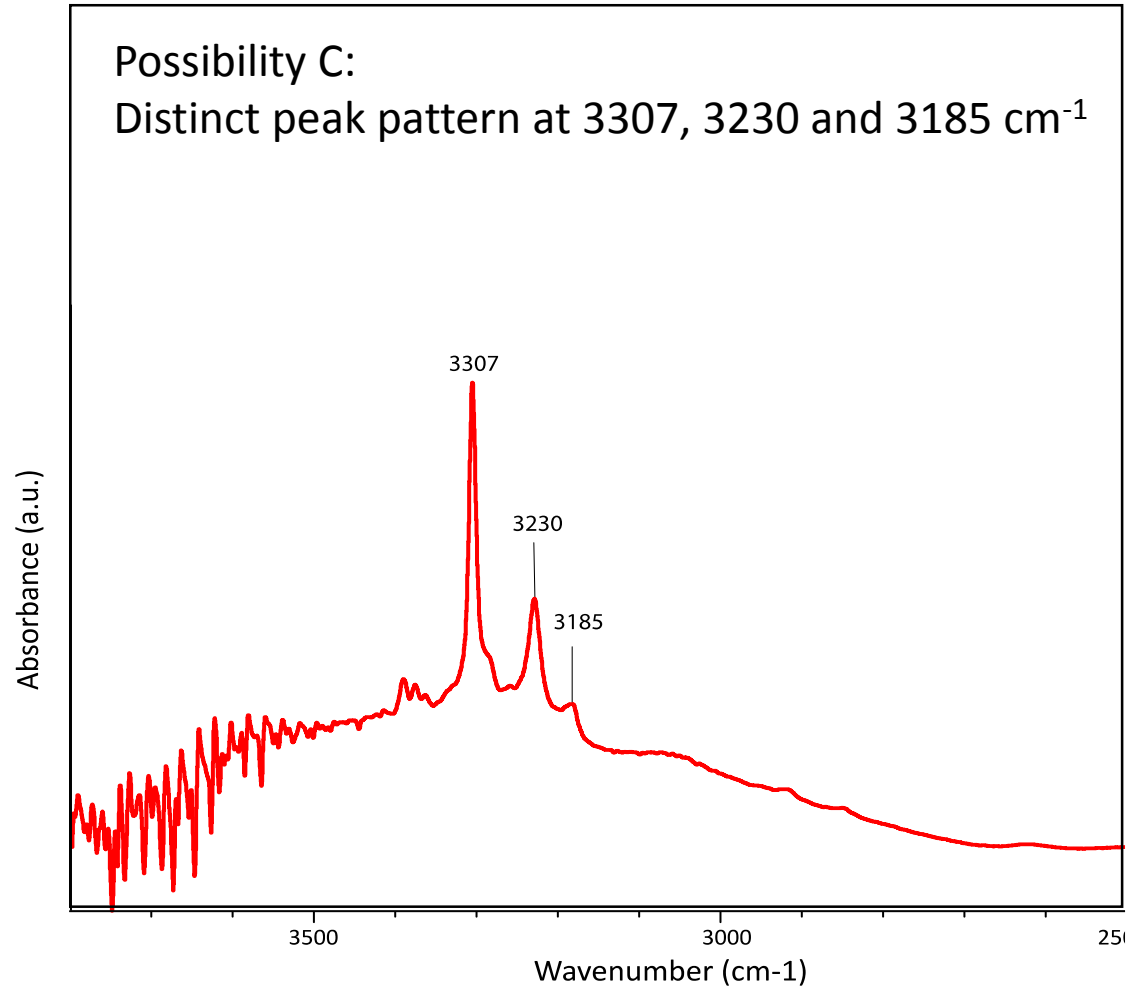
Spectra: SSEF

IR Spectra of Sapphires heated with Pressure



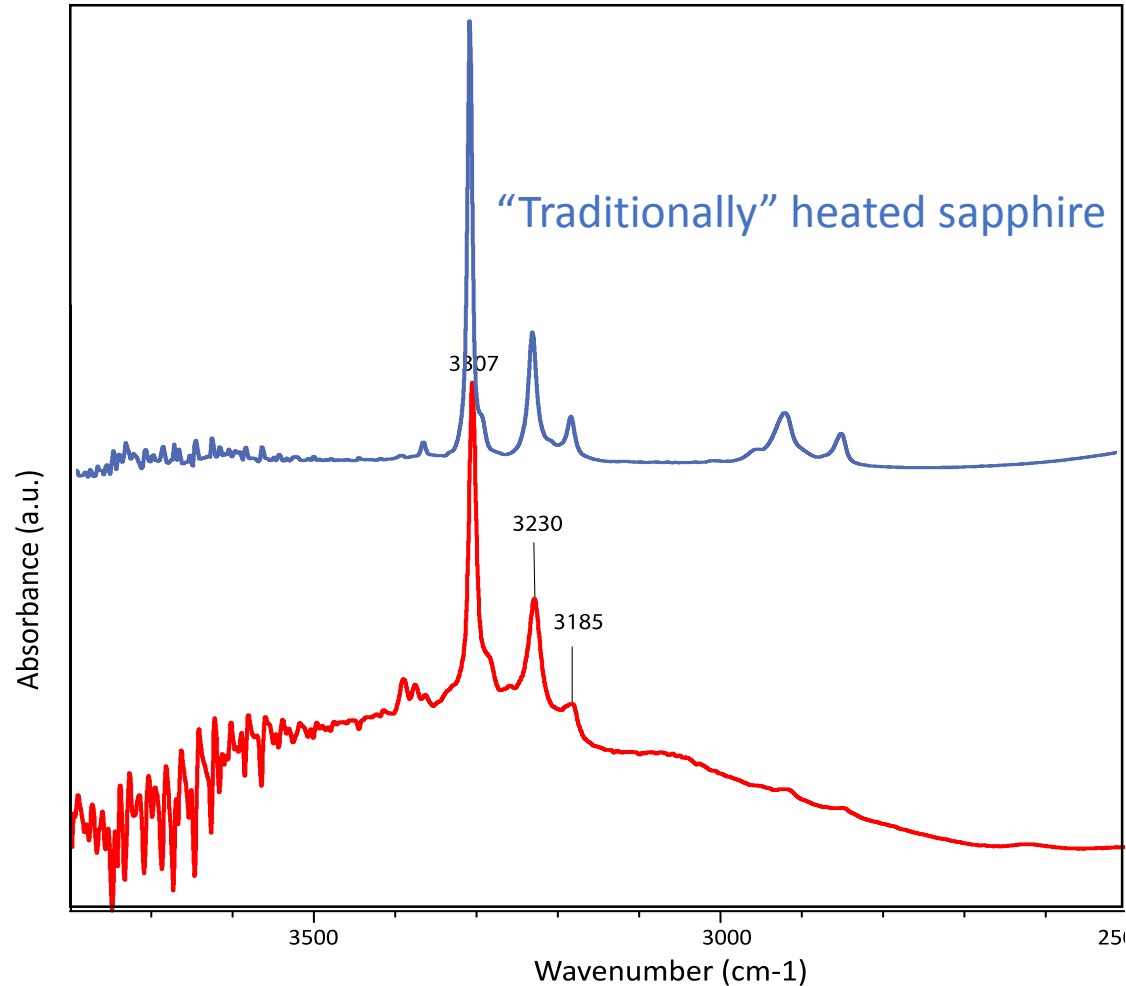
Similar pattern in untreated yellow sapphires from Thailand (Chanthaburi) and Australia (Queensland) (see Sangsawong et al. 2015) and in Ni-doped synthetic corundum.

IR Spectra of Sapphires heated with Pressure



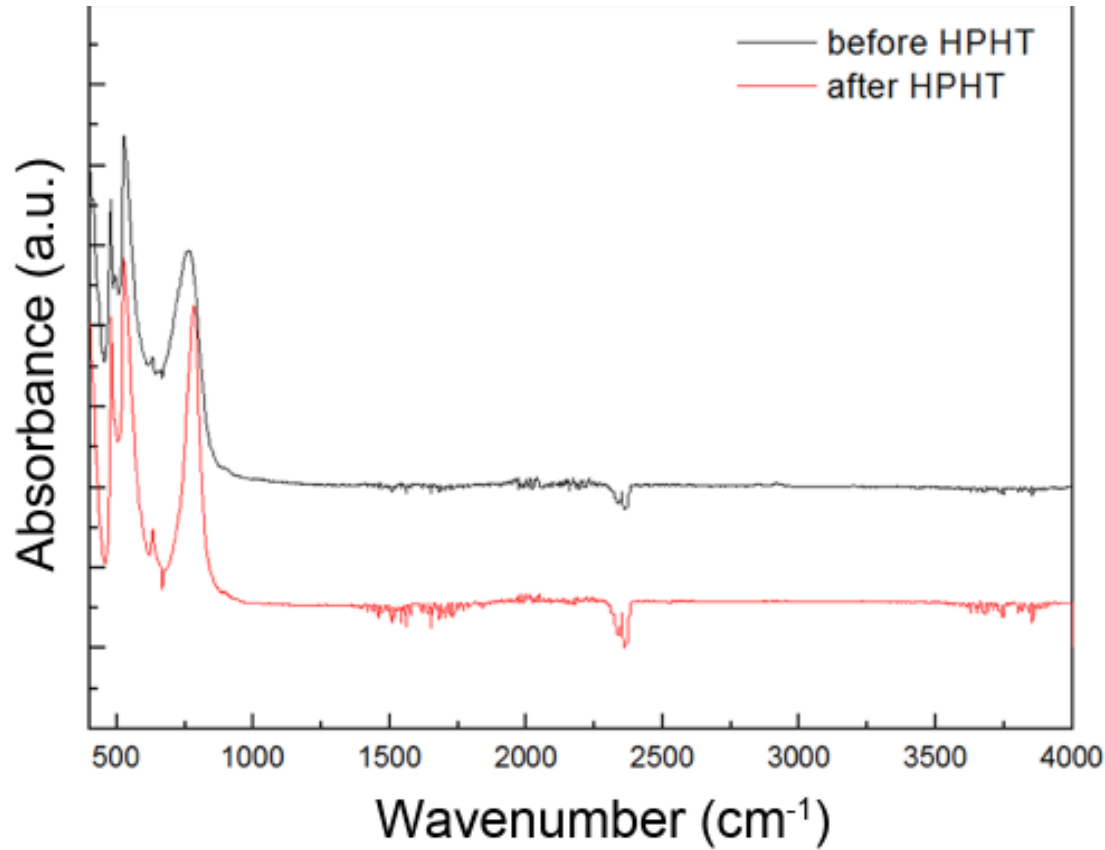
Spectrum: SSEF

IR Spectra of Sapphires heated with Pressure



The same spectrum is also characteristic for "traditionally" heated sapphires!

IR Spectra of Sapphires heated with Pressure



Song et al. 2015:

No feature at all in sapphire heated with real high pressure (1 GPa) !

Key challenges for detection

- No clear cut identification feature using microscope,
- Ultraviolet reaction, UV-Vis absorption, and trace element composition are not diagnostic for the treatment
- Great variability of FTIR spectra
- Many sapphires heated with pressure show IR spectra that are not diagnostic for the treatment

Questions regarding pressure heated sapphire

- Increased supply of sapphires on market?
- Inclusion damages?
- Fissure healing?
- Addition of foreign elements?
- Durability / stability issues?

Down to brass tacks



Q. Are there durability problems that result from this treatment?

A. Our studies revealed none.

Q. Does this treatment produce significant advantages in terms of improvements in clarity (fissure healing, etc.)?

A. The differences we have seen are generally slight and not unlike sapphires conventionally heated at high temperatures.

Q. Does this treatment significantly increase the supply of sapphire in the market?

A. To date, it has not.

Q. What percentage of stones that have been subjected to this treatment are currently identifiable by labs?

A. We simply do not know.

Q. Does this treatment warrant separate disclosure?

A. Based on current information, we believe it does not. But we reserve the right to change our minds if future evidence warrants it.

Fits perfectly Normal Heating Disclosure



Heating **with no** diffusion of colouring elements from external source and **with no** addition of a flux to fill or even “heal” fissures

Blue sapphires **heated with pressure**



all variations of heating methods are commonly summarised and disclosed only as **heated**



Heating **with** diffusion of colouring elements from external source to produce colour and/or assisted **with** a flux to fill or even “heal” fissures



Each different method is **specifically disclosed.**

Further challenge:

If a sapphire heated with pressure is subsequently heated again, the complex OH⁻ absorption band (left spectrum) disappears. It may even result in a FTIR spectrum resembling a traditionally heated sapphire (right spectrum).

