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Observations on the heat treatment of basalt-related blue sapphires

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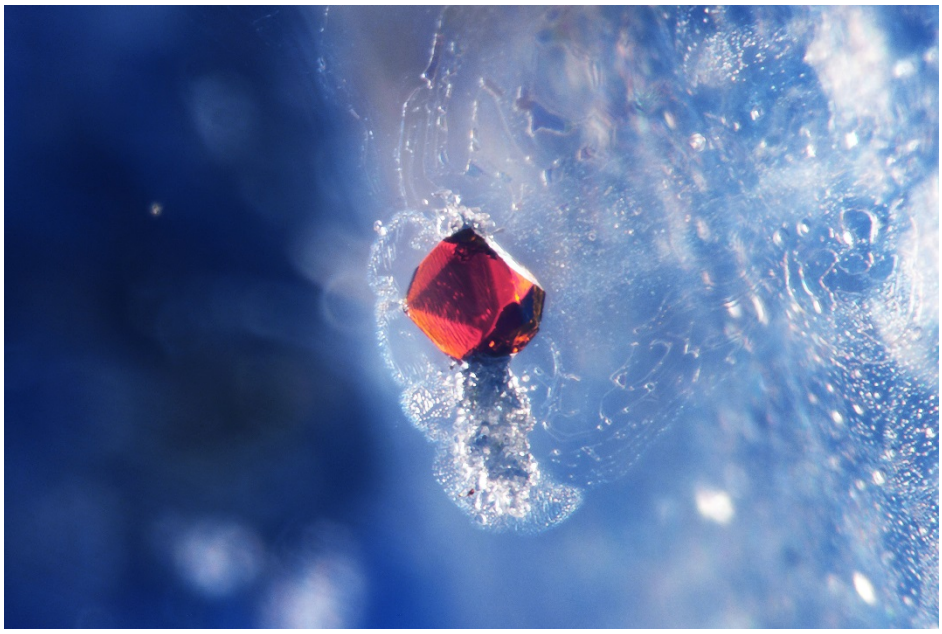

The dark red crystal, presumably pyrochlore, in this Cambodian blue sapphire changed to red-orange crystal with a surrounding partially healed fracture after low-temperature heat treatment, darkfield and fiber-optic illumination. FOV 1.05 mm. Photomicrograph by C. Khowpong © GIA.

Abstract

Basalt-related blue sapphires typically have an oversaturated blue color causing the stones to be too dark when faceted. Low-temperature heat treatment can lighten dark material. However, it is difficult to identify this treatment using standard gemological testing and microscopic examination. For instance, unheated sapphires are transported to the earth's surface by hot, basaltic magma which may have thermally altered their inclusions, causing them to look similar to those seen in artificially heated material. In this study, 50 basalt-related blue sapphires were heat treated in air (oxidizing atmosphere). Changes in color appearance, UV fluorescence, internal features, and spectroscopic properties post treatment were compared with the results before treatment to find suitable approaches for detecting heat treatment on blue sapphires from basalt-related deposits.

The main factors affecting the sapphires' response to heat treatment includes the temperatures employed and the duration of the treatment process. Initial experiments at temperatures of 500–1500°C for 7 hours showed that the blue color appears to lighten at 700°C and higher. Temperatures ranging from 700 to 1050°C were then selected for a more in-depth study on the effect of heating time with durations of 1.75, 7, and 28 hours. The results showed negligible change to a slight lightening of the blue color after treatment at 700°C, while an obvious lightening of the blue color occurred at 900 and 1050°C. Some mineral inclusions, iron stains, and partially healed fractures showed signs of alteration during these heating experiments, while needles and minute particles did not show any signs of change. All unheated samples studied were inert to short-wave ultraviolet radiation. After heating, most remained inert under short-wave UV, but a few samples exhibited a very weak chalky green fluorescence.

FTIR spectra obtained from the samples varied considerably, with differences in peak intensities before and after heating. Differences were also seen as the duration of heating was changed. In most cases, unheated blue sapphires from basalt-related deposits revealed the characteristic 3309 cm^{-1} series (sharp peaks at 3309, 3232 and 3186 cm^{-1}) in the FTIR spectrum with the intensity of 3232 cm^{-1} being much lower than that of 3309 cm^{-1}. After heating at 700°C and 900°C, the intensity of the 3309 cm^{-1} peak decreased and the 3232 cm^{-1} peak increased, respectively. However in most cases, some samples that initially showed a relatively intense 3232 cm^{-1} peak before treatment exhibited a more intense 3309 cm^{-1} peak and a less intense 3232 cm^{-1} peak post treatment. After heating at 1050°C for 1.75 hours, we recorded a decrease in the intensity of the 3309 cm^{-1} peak and an increase in the 3232 cm^{-1} peak, to the point where they were of almost comparable intensity. When subsequently heated for 7 and 28 hours, the intensity of the 3309 cm^{-1} peak increased and that of the 3232 cm^{-1} peak decreased.

UV-Vis-NIR spectra obtained from the samples heated at 900°C and 1050°C for 1.75, 7, and 28 hours showed a reduction in the height/intensity of the broad band centered at 580 nm related to an Fe^{2+}-Ti^{4+} intervalence charge transfer. This reduction is the root cause of the lighter color after heat treatment.

The results of this study showed that even with advanced testing, it is very challenging to separate basalt-related sapphires that have been artificially heated from natural unheated stones, owing to the variable results associated with the experimental temperatures and durations used. Inclusion studies may provide sufficient evidence in some cases, but even when comparing the inclusions scene before and after treatment, separation often remains challenging.

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1. Introduction

Heating is the most common treatment to improve color and/or clarity of corundum. The main factors that influence the changes in corundum are the temperatures employed, the duration of the treatment process, and the composition of the furnace atmosphere—reducing or oxidizing atmosphere (Nassau 1981, Emmett and Douthit 1993, Emmett *et al*. 2003, Emmett *et al*. 2017). According to the alteration of second-phase microcrystals, heat treatment can be classified into a high or low temperature process based on the dissolution of rutile for corundum. The term 'low-temperature' heat treatment is used when the dissolution of rutile particles into corundum does not occur at that temperature. The temperature boundary between low- and high-temperature heat treatment is roughly 1200–1350°C (Emmett *et al*. 2017, Themelis 2018).

Blue sapphires from basalt-related deposits, such as Australia, Thailand, Cambodia, and Nigeria, are found in the gem and jewelry trade. They typically have an oversaturated blue color causing the sapphires to be too dark when faceted (Hughes 2017). The color of these materials can be lightened with heat treatment at either low or high temperatures (Emmett *et al*. 2017, Nassau 1981, Themelis 2018). Proving whether a sapphire has been heat treated is often not simple. This is especially true for basalt-related blue sapphires which have experienced some heat naturally when they transport to the earth's surface. High temperature heat treatment can often be identified by melted or altered inclusions, internal diffusion, broken silk, or colored halos surrounding altered crystals (Kammerling *et al*. 1990, McClure *et al*. 2000, McClure *et al*. 2010). In addition, heat-treated corundum may show chalky bluish to greenish white fluorescence under short-wave UV radiation. Low-temperature heat treatment has much less effect on the sapphires' inclusion scenes making it very difficult to identify the treatment using only microscopic observation and fluorescence reaction under short-wave UV radiation (McClure *et al*. 2000). Fourier transform infrared spectroscopy (FTIR) is a useful tool to assist in the detection of heat treatment in corundum. The presence or absence of some FTIR features in the OH absorption region (3100-3600 cm^{-1}) may be used as evidence of heat treatment in some cases (Smith 1995, Beran and Rossman 2006, Saeseaw *et al*. 2018).

The specific conditions used in the trade for these heat treatment processes are often unknown to the gemological laboratories. Therefore, in this study, basalt-related blue sapphires were heat treated under various temperatures and time for heating in air (oxidizing condition) to see which experimental conditions improved the color of these materials. Changes in the gemological and spectroscopic properties of basalt-related blue sapphires before and after heat treatment were used to determine if diagnostic tests can detect heat treatment, particularly the low temperature process.

2. Materials and methods

2.1 Samples

Fifty basalt-related blue sapphires were selected for heat treatment in air at different temperatures and durations of the process. GIA field gemologists collected the samples in the mines from various locations including Australia, Cambodia, Nigeria, and Thailand. These blue sapphires were fabricated for two different purposes:

1) 20 samples were selected for documenting their inclusions, in particular, with one or more polished windows regardless of the orientation to the c-axis.

2) 30 samples were selected as optical wafers with two polished surfaces perpendicular or parallel to the c-axis using GIA's corundum c-axis device for sample preparation (Thomas, 2009). These samples possess a sufficiently large and clean area to get high quality spectra and to observe the alteration of inclusions.

2.2 Heat treatment process

Prior to heating, the samples were cleaned with acetone and placed in an ultrasonic bath. The heating experiment were performed in air without any additives, using a KSL-1800X electric furnace for experiments in Section 3A and Annex A, and a Thermolyne FB1400 benchtop 1100°C muffle furnace manufactured by Thermo Scientific for experiments in Section 3B. The samples were placed on a high purity alumina (Al_2O_3) plate to avoid surface contamination. Multiple heat treatments were applied with a set of samples for each variable, either heating temperatures or durations of the process. During heating, the temperature was increased from room temperature to the temperature employed with a ramp rate of 5 or 10°C/min then held at that temperature at a given heating duration. After that, the samples were allowed to cool down to room temperature rapidly. The detection of heat treatment was investigated by observing the change in color appearance, internal features, UV fluorescence reaction, FTIR and UV-Vis-NIR spectra, comparing before and after heat treatment.

2.3 Instrumentation

2.3.1 Standard gemological testing

A Rayner refractometer (yttrium-aluminum-garnet prism) equipped with a near sodium-equivalent light source was used to measure refractive index and birefringence. Long-wave (365 nm) and short-wave (254 nm) UV lamps were used to observe fluorescence reactions.

2.3.2 Sample photography

A Canon EOS 5D camera, with a Canon Macro MP-E 65 mm lens adapted to a camera stand, was used to document the color of the samples before and after the heat treatment process. Photographs were taken under exactly the same lighting conditions, with the reference samples being placed in a Logan Electric Tru-View 810 Color Corrected Light Box (5000 K 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 photos were taken of wafers cut perpendicular or parallel to the c-axis, the color of the samples in the photographs taken using transmitted light may be considered as representative of the color of a nearly pure the ordinary (o-) and extraordinary (e-) rays.

Photomicrographs of internal features were captured at different magnifications with a Nikon SMZ 18 system and a Nikon SMZ 1500 system using dark-field, bright-field, diffused and oblique illumination, together with a fiber-optic light source when necessary. It should be noted that the field of view information in the captions was calculated by taking the magnification power of the microscope into consideration.

2.3.3 UV-Vis-NIR spectroscopy

Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were collected with a Hitachi U-2900 spectrophotometer specially modified at GIA to include a rotatable polarizer to allow the separate collection of both o-rays and e-rays. A wavelength resolution of 1.5 nm was used. The spectra obtained were corrected by calculating the reflection loss from the index of refraction data and then converted to

absorption coefficient (α, cm^{-1}) using $\alpha = 2.303A/d$, where A is absorbance and d is the path length in centimeters. Three replicate spectra were collected for each sample.

2.3.4 Fourier transform infrared absorption spectroscopy (FTIR)

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 4× beam condenser accessory. Resolution was set at 2 cm^{-1} with 0.964 cm^{-1} data spacing. The spectra obtained were converted to absorption coefficient (α, cm^{-1}) using $\alpha = 2.303A/d$. Three replicate spectra were collected for each sample.

2.3.5 Raman spectroscopy

To identify mineral inclusions, Raman spectra were obtained using a Renishaw inVia Raman microscope fitted with a 514 nm argon-ion laser. The spectra were collected in the range of 100 and 1500 cm^{-1}. The accumulation time was set at a minimum of 5 until the signal to noise ratio of the spectra was adequate. The calibration was performed using the 520.5 cm^{-1} line of a silicon wafer. In all cases, the RRUFF database was used as a reference when identifying inclusions. Spectral comparisons were performed using Renishaw Wire (version 3.4) and/or Thermo Galactic Spectra ID (version 3.02) software.

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

Chemical analysis was carried out using LA-ICP-MS technology with a Thermo Fisher Scientific iCAP Q inductively coupled plasma-mass spectrometer (ICP-MS) and a Q-switched Nd:YAG Laser Ablation (LA) device operating at a wavelength of 213 nm. Laser conditions consisted of 55 µm diameter laser spots, a fluency of around 10 J/cm^2, and a 15 Hz repetition rate. Twelve spots were analyzed on each wafer. ICP-MS was operated using the forward power at approximately 1350 W and the typical nebulizer gas flow at ~ 0.80 L/min. Helium was used as the carrier gas in the laser ablation unit and the flow rate was also set at ~ 0.80 L/min. The criteria for the alignment and tuning sequence were to maximize Be counts and to keep the ThO/Th ratio below 2%. A special set of synthetic corundum reference standards was used for quantitative analysis (Stone-Sundberg *et al*. 2017). All elemental measurements were normalized on Al as the internal elemental standard. This value approximates to the chemical composition of corundum.

3. Results and discussion

The main factors that influence the changes in corundum are the temperatures employed, the atmosphere of the furnace and the duration of the treatment process. Since the purpose of heat treatment was to lighten the oversaturated blue color of the samples, heating was carried out in air (oxidizing atmosphere) to reduce Fe^{2+}-Ti^{4+} intervalence charge transfer absorption (Emmett and Douthit, 1993).

In this study, the effect of both temperature and length of the heat treatment process were investigated on basalt-related blue sapphires from various sources, including Australia, Cambodia, Thailand, and Nigeria:

A) The initial experiment consisted of heat treating the blue sapphires at different temperatures ranging from 500–1500°C with durations of 7 hours to observe the change in color appearance (*4 samples*).

B) Temperatures ranging from 700 to 1050°C for durations of 1.75, 7, and 28 hours were selected for a more in-depth study on the change of blue sapphires caused by heat treatment (*46 samples*).

Different detection methods, either standard gemological testing or advanced instruments, were used to determine if any tests can distinguish untreated basalt-related blue sapphires from treated materials. In addition, seven basalt-related blue sapphires were also heat treated using a high temperature process at 1500°C for 7 hours to document the alteration of internal and external features, as shown in Annex A.

Part A: Heating temperatures (500 to 1500°C)

Color appearance: In the preliminary study, two blue sapphires from Thailand and Cambodia, respectively, were heat treated at temperatures ranging from 500 to 1500°C for 7 hours. Figure 1 and Figure 2 show color-calibrated photos of the samples before and after heating at different temperatures. The blue color of the samples appeared to lighten at 700°C and above. Thai sapphire sample 3502 (Figure 1) showed more greenish color when the blue color was reduced after heating. In addition, the light yellow color of the iron stain, probably limonite, on the surface of Cambodian sample 2388 in Figure 2 changed to brownish red of hematite when heated at 700 and 1100°C. It subsequently changed to yellow after heating at 1300°C, then decomposed after heating at 1500°C (close to the melting point of hematite at 1565°C, Lide 2000). The change in color of the iron stain may be used as a clue for heat treatment in corundum (Koivula 2013, Sripoonjan 2016).

Magnification: Microscopic examination revealed no alteration to the polished surface of the samples after heating between 500 and 1100°C. Melted/droplet surfaces and pits were found after heating at 1300°C. Since these four samples are optical wafers, they contain a limited number of internal features including strings of particles and short needles, partially healed fractures, bands of minute particles, and fluid inclusions. Microscopic examination revealed a slight alteration of inclusions after post treatment. More details on the effect of heat treatment on internal features will be shown later in Section 3B and Annex A.

Fluorescence: If corundum has been heat treated at high enough temperature to re-dissolve rutile particles/needles, a chalky fluorescence reaction can be observed under short-wave UV radiation. This fluorescence results from the charge transfer transition from the valence band of the corundum lattice to the Ti^{4+} ion (Emmett *et al*. 2017). The presence of chalky (whitish to green) fluorescence is usually used to confirm heat treatment in metamorphic blue sapphires. However, basalt-related blue sapphires may respond differently as they were exposed to some heat naturally when they traveled to the earth's surface. In the experiments, no chalky fluorescence was observed on these four samples either before or after treatment over a wide range of temperatures from 500 to 1500°C. This is possibly because high Fe concentrations in these basalt-related blue sapphires can quench chalky fluorescence (Emmett *et al*. 2017).

FTIR spectroscopy: This instrument can sometimes be used to help identify heat treatment in corundum. Sample 8602 was chosen as a representative example. Its FTIR spectra before and after heat treatment at different temperatures are shown in Figure 3. They were collected at the same position on the sample for comparison. Unheated blue sapphires from basalt-related deposits frequently revealed the characteristics of the 3309 cm^{-1} series, consisting of three sharp peaks at 3309, 3232 and 3186 cm^{-1} (Figure 3, Emmett and Scarratt *et al*., 2017). The 3309 cm^{-1} peak is typically strongest among these three sharp peaks. The IR features of the 3309 cm^{-1} series are related to the stretching vibration of the OH bond in alumina containing Ti and H impurities (Moon and Phillips 1991). As seen in Figure 4, the intensities of the 3309 cm^{-1} peak decreased and the 3232 cm^{-1} peak increased after heating from 500 to 1100°C. The intensities of the 3309 and 3232 cm^{-1} peaks significantly decreased and subsequently disappeared after heating at 1300 and 1500°C, respectively. The reduction of the intensities of the 3309 cm^{-1} peak in basalt-related blue sapphires after treatment corresponds with

previous reports (Sutthirat *et al*. 2006, Abduriyim 2006 as cited in Hughes R.W. 2017). In this study, two samples—one from and Thailand and another from Cambodia—also showed similar results, whereas another Thai blue sapphire did not display any IR features either before or after heating at all experimental temperatures.

UV-Vis-NIR spectroscopy: Representative UV-Vis-NIR spectra of basalt-related blue sapphires are shown in Figure 5 and Figure 7 showing typical Fe^{3+} related absorption peaks at 377, 388, and 450 nm (Ferguson and Fielding 1972 and 1997, Krebs and Maisch 1971), and an absorption band centered at 580 nm in the o-ray which is attributed to the Fe^{2+}-Ti^{4+} intervalence charge transfer for producing blue color in corundum (Dubinsky and Emmett 2013). In addition, this sample showed the absorption band centered at around 890 nm which is typically seen in blue sapphires from basalt-related deposits. This band is believed to be related to Fe clusters, however, the cause of the 890 nm absorption band is not known (Emmett *et al*. 2017). A band centered at 580 nm in the o-ray was significantly reduced which corresponds with the lightening of blue color after heating (Figure 1 and Figure 2**)**. Other Cambodian and Thai sapphires showed similar alteration. It should be noted that the broad band at 890 nm is partially overlapped with the of Fe^{2+}-Ti^{4+} band, and maximum peak positions were slightly shifted from 890 nm at different treatment conditions. To observe the change in the 890 nm absorption band only, the o-ray spectra of the samples in Figure 5 and Figure 7 were subtracted with a pure Fe^{2+}-Ti^{4+} absorption spectrum obtained from synthetic blue sapphire (Figure 6). The differential spectrum showed the position of maximum peaks being at 890 nm for all spectra. Two Cambodian sapphires, samples 8602 (Figure 6) and 2388, showed a slight decrease in intensity of the 890 nm band after heating, whereas two Thai sapphires, samples 7245 (Figure 8) and 3502, showed an increase in the intensities of the 890 nm band after heating. The e-ray spectra of the samples also changed when comparing before and after treatment. A decrease in intensities of the broad band in the red and near infrared was recorded. The band positions also shifted from 770 nm to 870 nm (Figure 5, bottom) and from 750 to 885 nm (Figure 7, bottom) after heating. The higher the temperature employed, the longer the wavelength of the band was recorded. The broad band in the red and near infrared for the e-ray spectrum of basalt-related blue sapphires is most likely from the combination of Fe^{2+}-Ti^{4+} intervalence charge transfer (at 700 nm) and Fe cluster absorption bands. Band shift after heating is possible in that the reduction of the Fe^{2+}-Ti^{4+} absorption band from treatment resulted in the Fe cluster band being dominant. Three other samples also showed the shift in band position and a decrease in the intensities of the broad band in the red and near infrared of e-ray spectra.

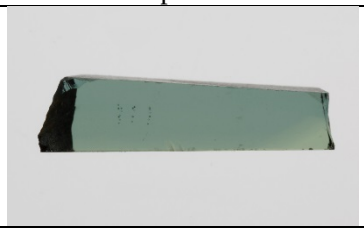
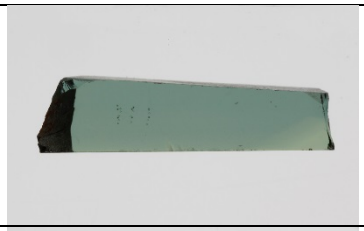
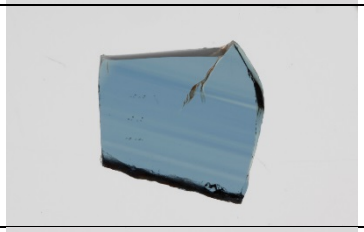
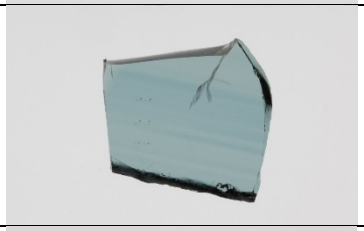
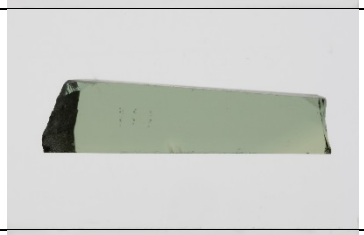
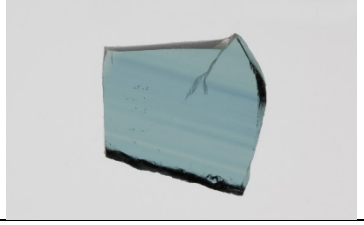
Sample	3502 (Thailand) Orientation: perpendicular to c-axis	7245 (Thailand) Orientation: parallel to c-axis
Before heating		
After heating at:		
500°C		
700°C		
900°C		
1100°C		
1300°C		
1500°C		

Figure 1: Color-calibrated photos of Thai blue sapphires before and after heating at different temperatures for 7 hours. Photos by S. Sangsawong © GIA.

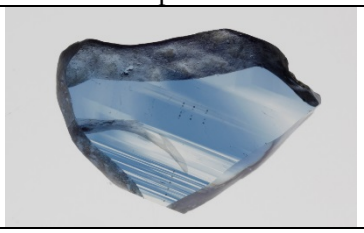
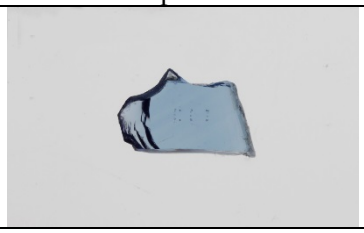
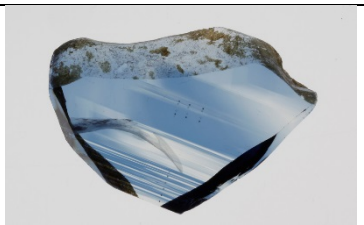
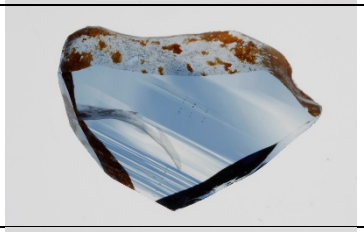
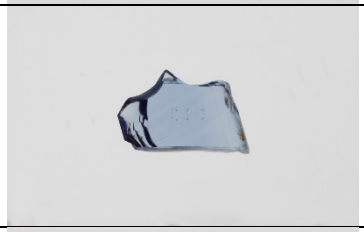
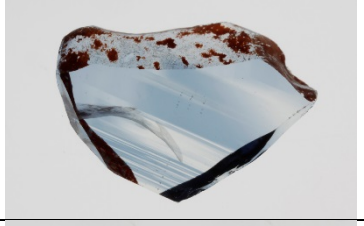
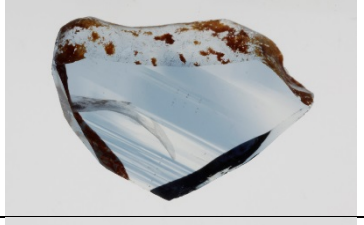
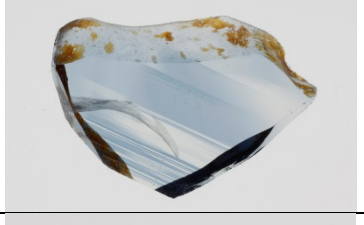
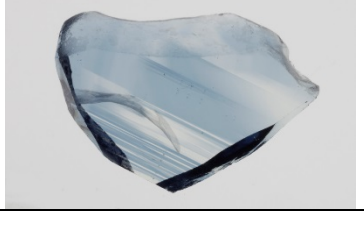
Sample	2388 (Cambodia) Orientation: parallel to c-axis	8602 (Cambodia) Orientation: parallel to c-axis
Before heating		
After heating at:		
500°C		
700°C		
900°C		
1100°C		
1300°C		
1500°C		

Figure 2: Color-calibrated photos of Cambodian blue sapphires before and after heating at different temperatures for 7 hours. Photos by S. Sangsawong © GIA.

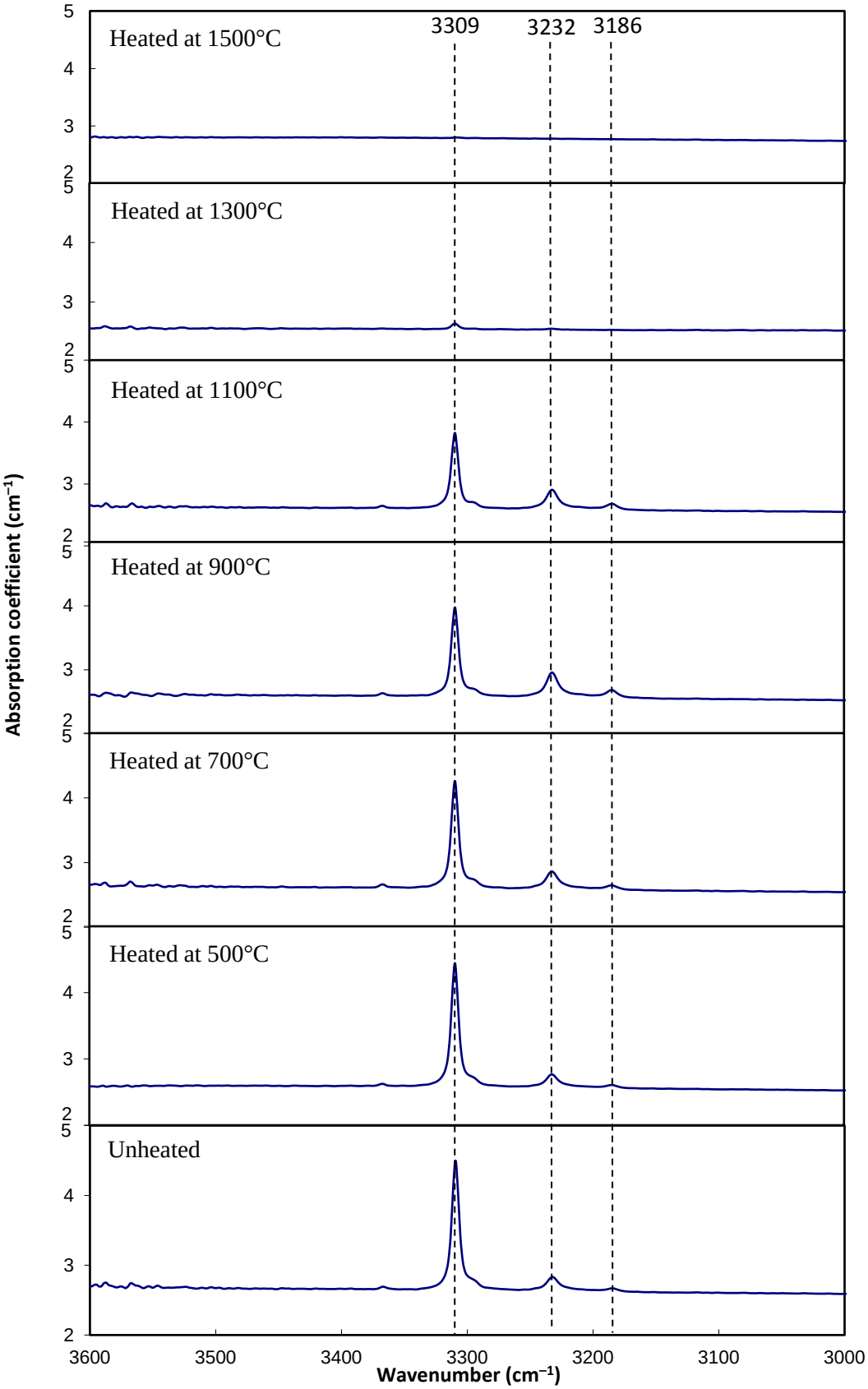


Figure 3: FTIR spectra of sample 8602 (Cambodia) before and after heating at different temperatures between 500 and 1500°C for 7 hours.

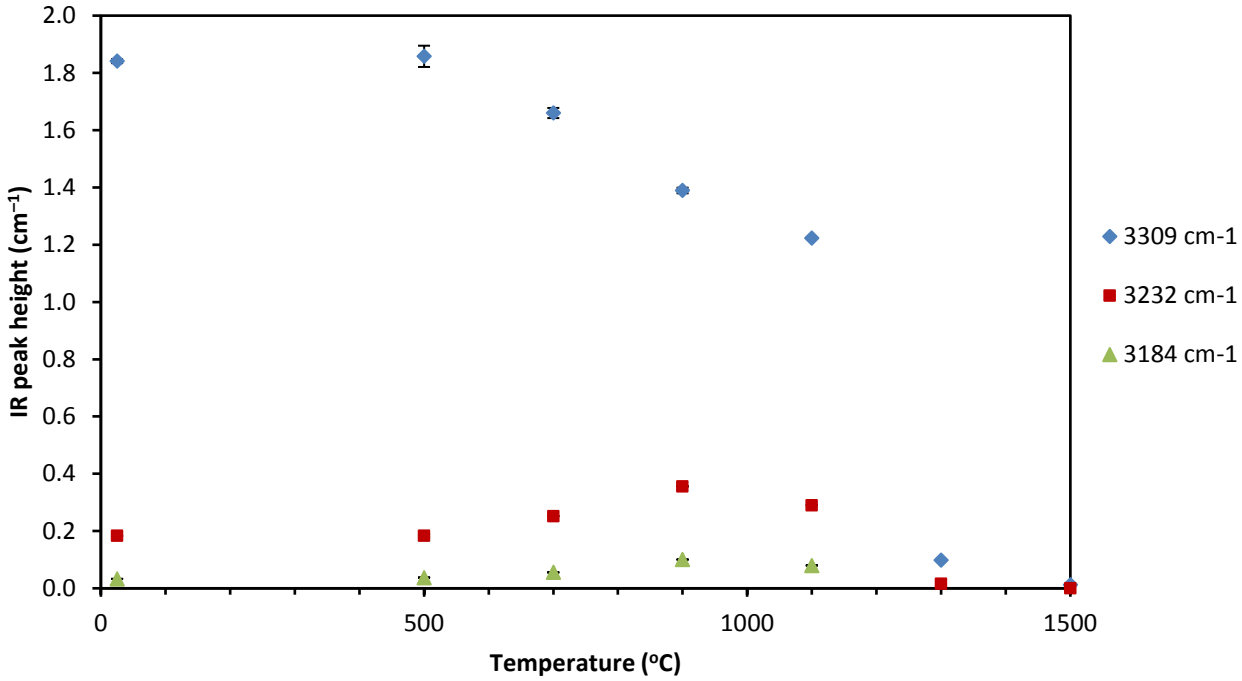


Figure 4: Plot of FTIR peak height of sample 8602 (Cambodia) before and after heating at different temperatures between 500 and 1500°C for 7 hours.

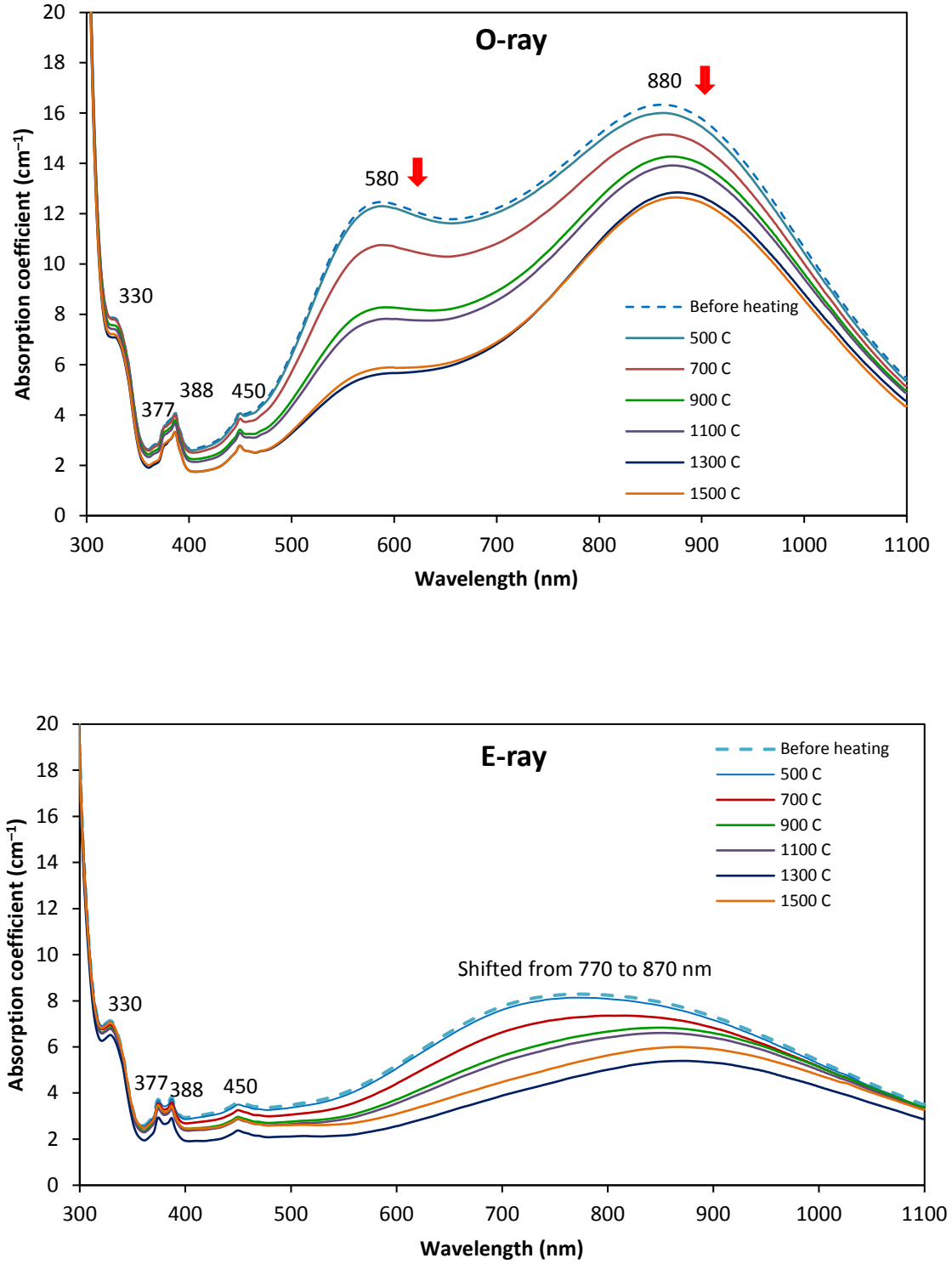


Figure 5: UV-Vis-NIR spectra of sample 8602 (Cambodia) with wafer plane parallel to c-axis, before and after heating at different temperatures between 500 and 1500°C for 7 hours. Optical path length 1.036 mm, α(max) 34 cm^{-1}.

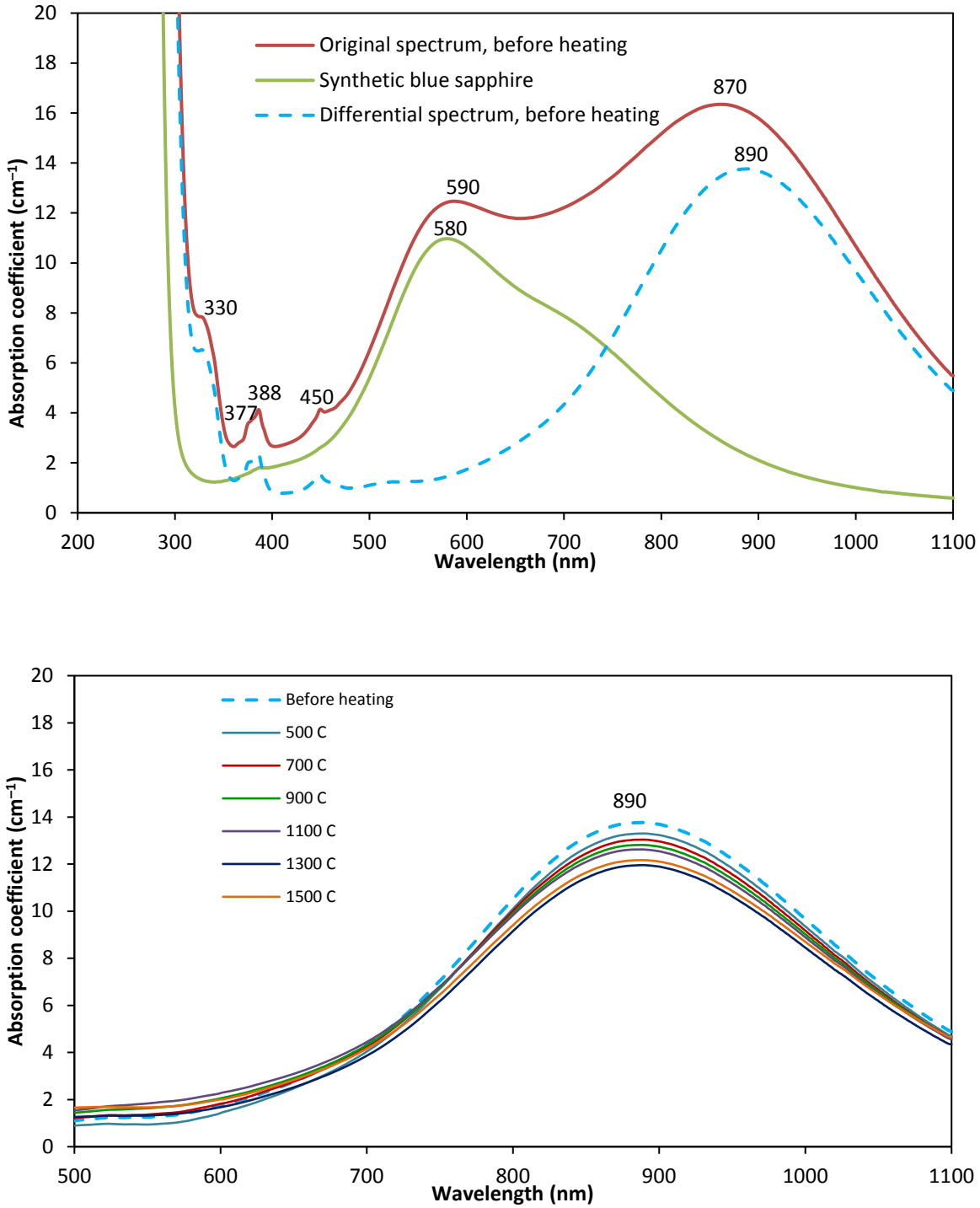


Figure 6: *Top*, the original UV-Vis-NIR spectrum of sample 8602 before heating (—), pure Fe^{2+}-Ti^{4+} absorption spectrum obtained from synthetic blue sapphire (—), and the differential spectrum of these two spectra (---). *Bottom*, these absorption spectra are from the differential of o-ray spectra from sample 8602 in Figure 5 before and after heating at different temperatures and an o-ray spectrum of pure Fe^{2+}-Ti^{4+} pair from synthetic blue sapphire.

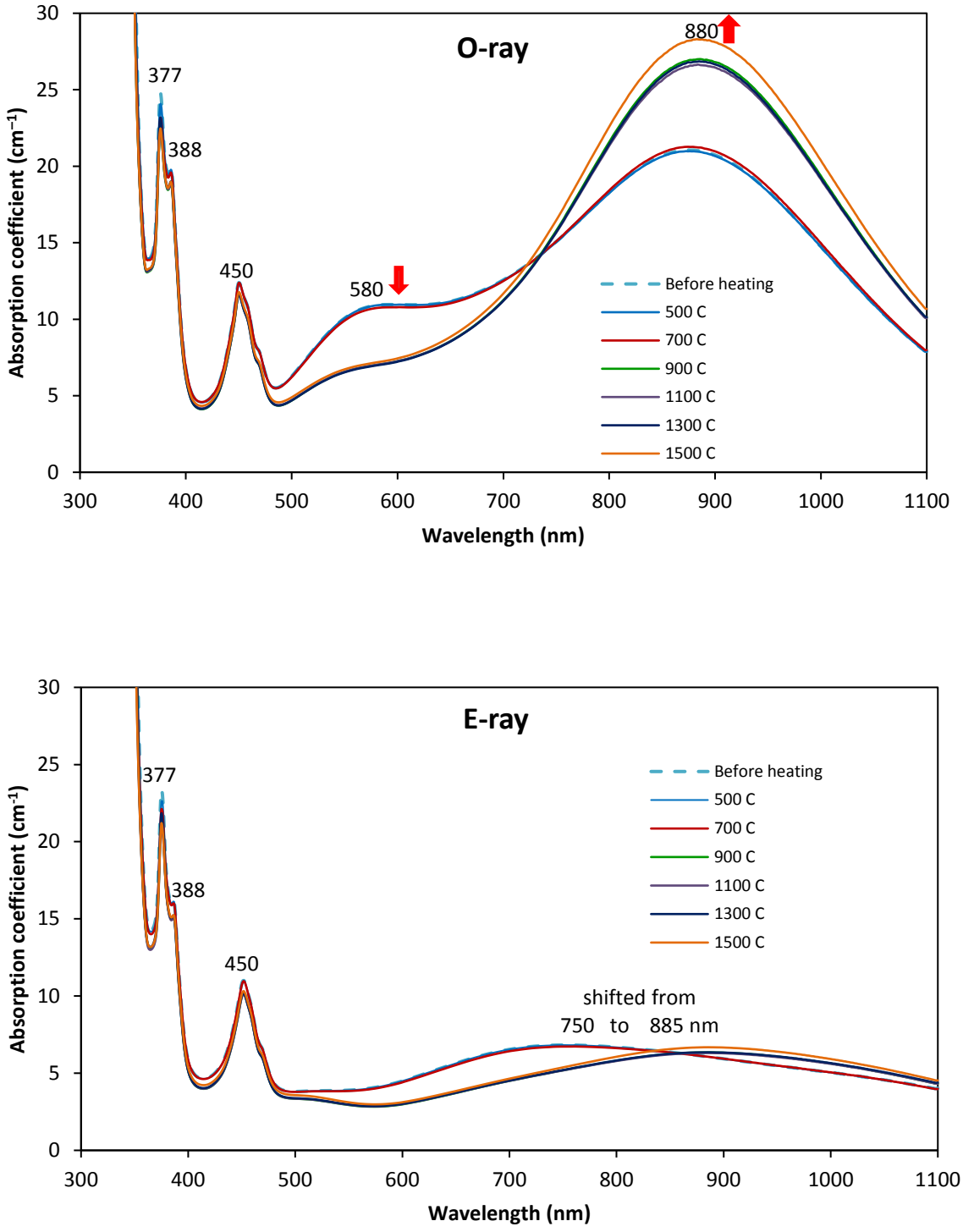


Figure 7: UV-Vis-NIR spectra of sample 7245 (Thailand) with wafer plane parallel to c-axis, before and after heating at different temperatures between 500 and 1500°C for 7 hours. Optical path length 1.636 mm, α(max) 22 cm^{-1}.

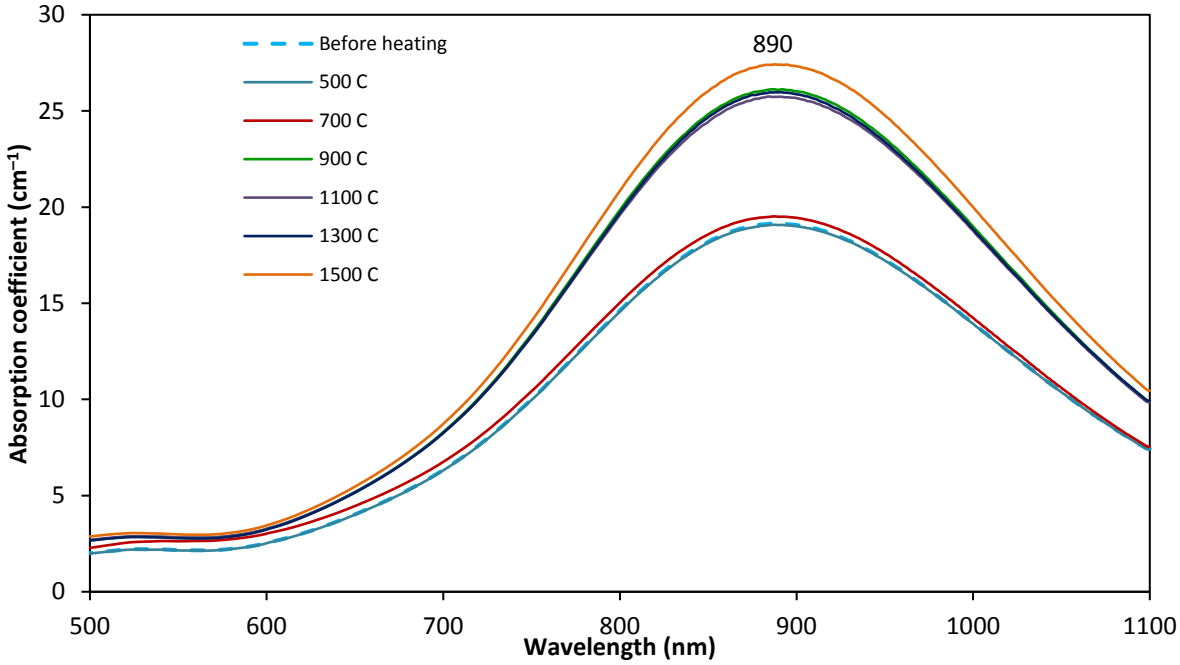


Figure 8: The resulting differential UV-Vis-NIR spectra of sample 7245 are from the o-ray spectra in Figure 7 and an o-ray spectrum of pure Fe^{2+}-Ti^{4+} pair from synthetic blue sapphire.

When blue sapphires were heat treated in air (oxidizing environment), the lightening of blue color (Figure 1 and Figure 2) resulted from the oxidation of Fe^{2+} to Fe^{3+} and the reduction of Fe^{2+}-Ti^{4+} pairs (Figure 5 and Figure 7). The higher the temperature employed, the more lightening of blue color was observed. The loss of hydrogen was also observed with the decrease in peak intensity of the 3309 cm^{-1} series when heated between 500 and 1300°C, and disappeared after heating at 1500°C (Figure 3 and Figure 4). With increasing temperature, the hydrogen moves around from site to site until it is diffused completely out of the corundum crystal entirely, as there are no OH absorption features in the FTIR spectra (Emmett 2011, El-Aiat and Kröger 1982). Also, the relative intensities of 3309, 3232, or 3186 cm^{-1} were changed (Figure 4). To lighten the blue color, rapid cooling is necessary in order to prevent the reform of the dissociated Fe^{2+}-Ti^{4+} pair in higher concentration (Emmett *et al*. 2017)**.**

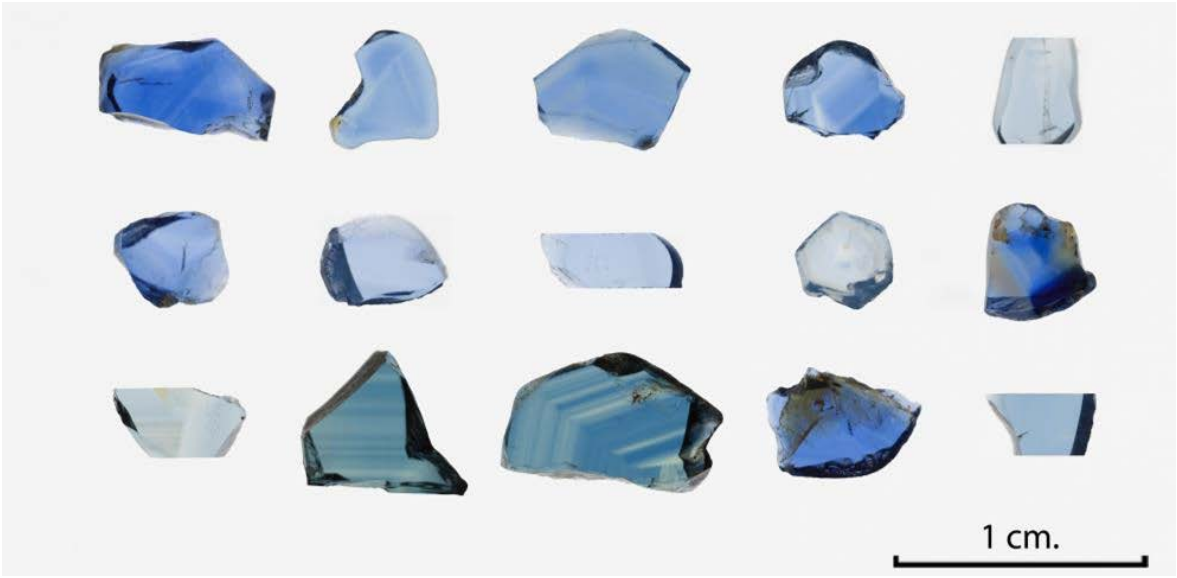
Part B: Durations of heat treatment process (1.75 to 28 hours) at experimental temperatures ranging from 700 to 1050°C

As shown in Figure 1 and Figure 2, the blue color of the materials appeared to lighten after heating at 700°C for 7 hours. Temperatures ranging from 700, 900, and 1050°C were selected for a more in-depth study on the effect of heating time on color appearance, fluorescence reaction, alteration of inclusions, and spectroscopic properties of basalt-related blue sapphires. At a given temperature, the heating times of the experiments were chosen at 1 hour 45 minutes (1.75 hours), 7 hours (duration used in Section 3A), and 28 hours.

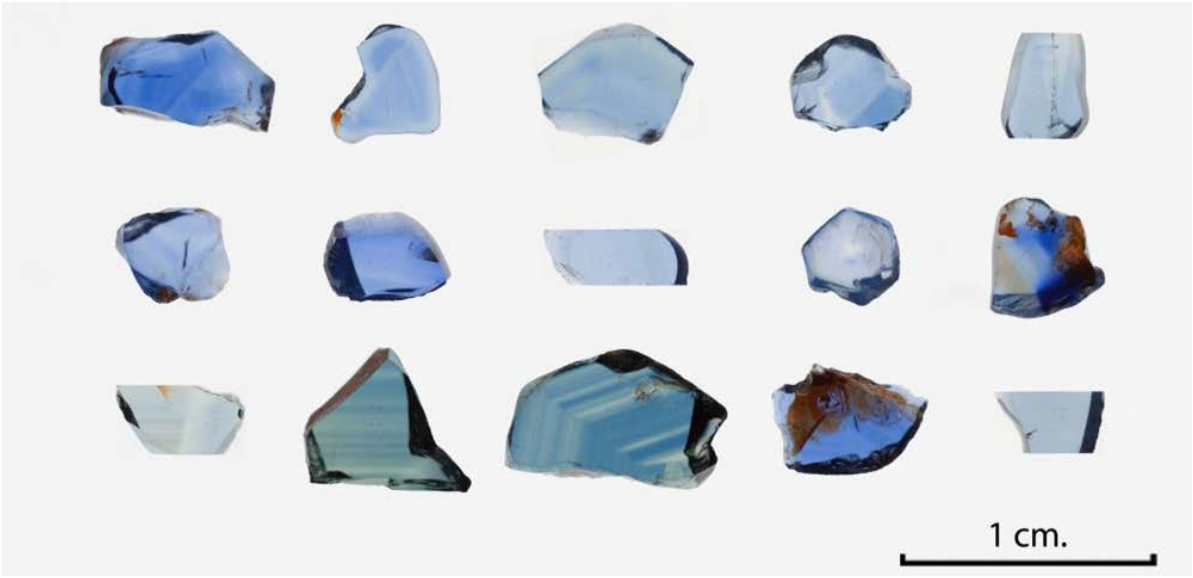
Color appearance: When heated at 700 °C (Figure 9) for durations ranging from 1.75 to 28 hours, a negligible change to a slight lightening of the blue color was observed in most samples. Interestingly, three out of 15 blue sapphires noticeably changed after treatment at 700°C for 28 hours to a more intense blue. Lightening of the blue color was obvious when heated at 900 and 1050°C in a range of durations used in the experiment, however, these samples showed a negligible change to a slight lightening in blue color when using different experiment durations (Figure 10 and Figure 11). The results indicated that color enhancement is strongly affected by heating temperature and slightly different between heating durations of 1.75, 7, and 28 hours at experiment temperature.

Magnification: As they were heated at relatively low temperature, there is no sintered or melted surfaces observed on these treated stones. Typical inclusions seen in basalt-related blue sapphires were selected for comparisons before and after heat treatment. Microscopic observation did not show any signs of change to milky bands (Figure 12), growth tubes (Figure 13), needles, and minute particles (Figure 14) at the experimental temperatures. As mentioned previously, the color of the iron stain looked darker/stronger after heating at and above 700°C (Figure 15, Figure 16). Minor alteration to fingerprints was detected after treatment between 700 to 1050°C (Figure 16, Figure 17, Figure 18). Some minerals, such as ferrocolumbite (Figure 19) and unidentified colorless or red crystals (Figure 20, Figure 21, Figure 22), showed signs of alteration at experimental temperatures, whereas some mineral inclusions did not alter, such as feldspar (Figure 23), zircon (Figure 24), molybdenite (Figure 25), and nepheline (Figure 26). Fluid inclusions (Figure 27) and fluid along fractures (Figure 28) sometimes changed from transparent to whitish forms after heating. Thin films negligibly or slightly changed after heating (Figure 29, Figure 30). Two-phase inclusions showed trapped gas bubbles after heating (Figure 31). It should be noted that insignificant changes in inclusions were observed with increased heating durations from 1.75 hours to 7 and 28 hours.

In some cases, the alteration of inclusions may provide sufficient evidence for detecting low-temperature heat treatment, however, even when comparing these internal features before and after heat treatment, the separation of unheated basalt-related blue sapphires from heat treated materials often remains challenging. In addition, some samples were heat treated using high temperature process at 1500°C in order to record the alteration of internal and external features for documentation in Annex A. Many altered inclusions caused by heat treatment were observed, such as melted solid inclusions, internal diffusion, broken needles, discoid fractures surrounded the crystals, as well as melted/droplet surfaces.

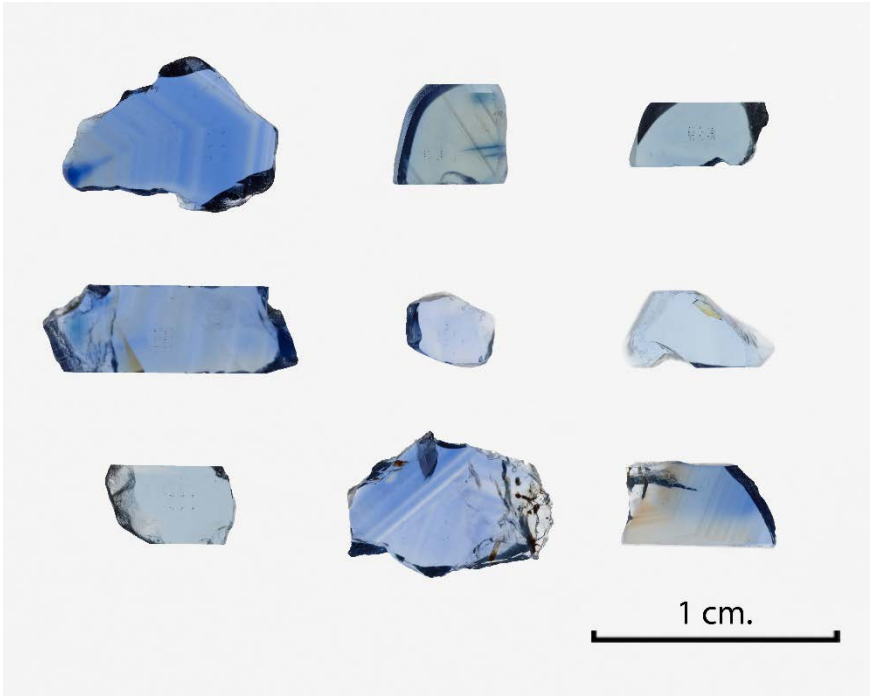


Before heating

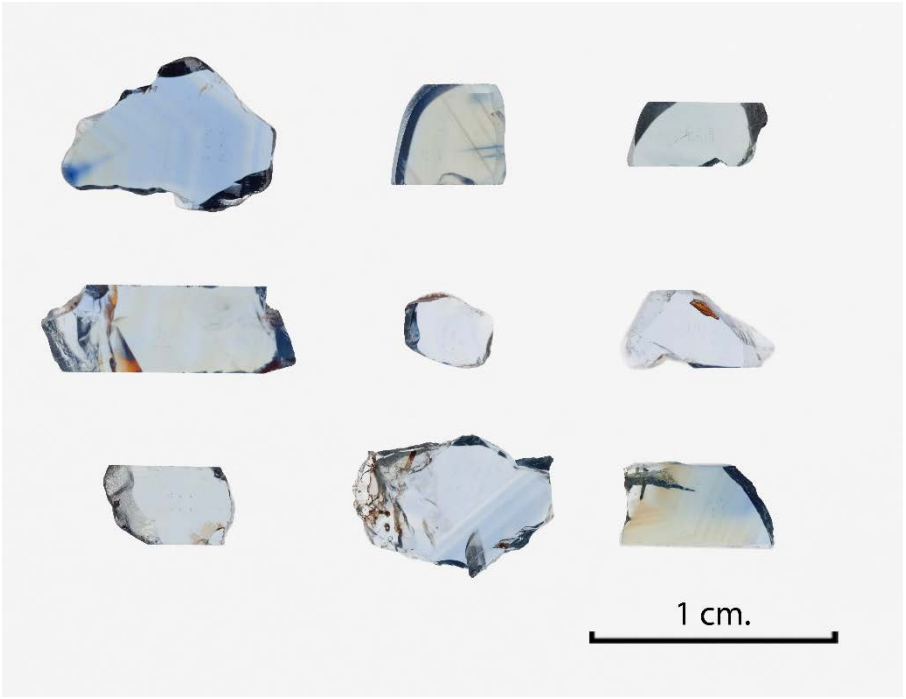


After heating at 700 °C for 28 hours

Figure 9: Color-calibrated photos of basalt-related blue sapphires, fabricated as optical wafers, before and after heating at 700°C for 28 hours. Photos by S. Engniwat © GIA.

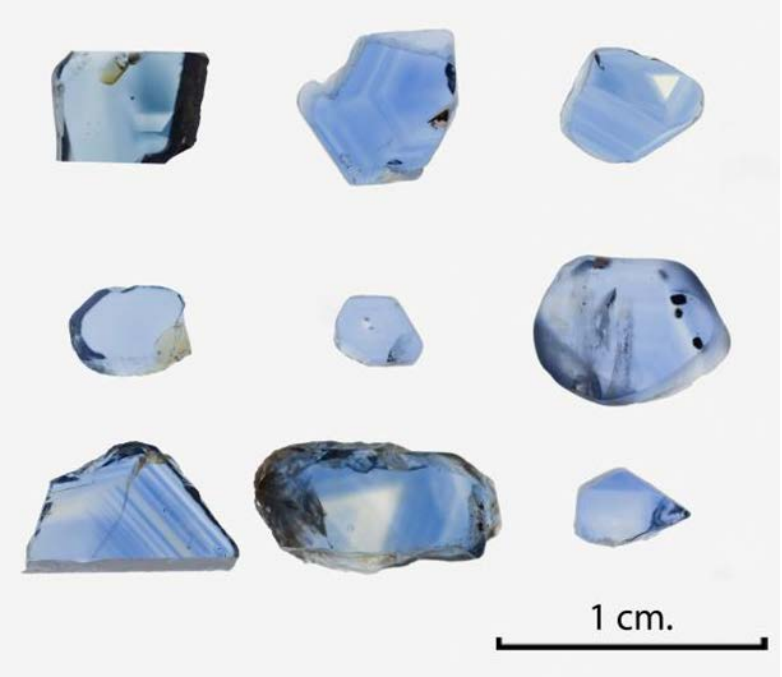


Before heating

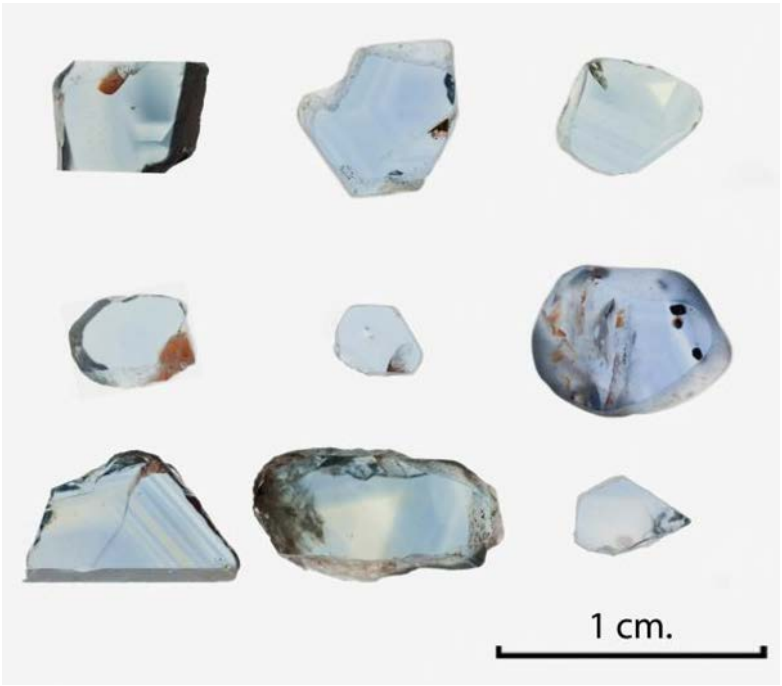


After heating at 900 °C for 28 hours

Figure 10: Color-calibrated photos of basalt-related blue sapphires, fabricated as optical wafers, before and after heating at 900°C for 28 hours. Photos by S. Engniwat © GIA.



Before heating



After heating at 1050 °C for 28 hours

Figure 11: Color-calibrated photos of basalt-related blue sapphires, fabricated as optical wafers, before and after heating at 1050°C for 28 hours. Photos by S. Engniwat © GIA.

Before heating ***After heating***

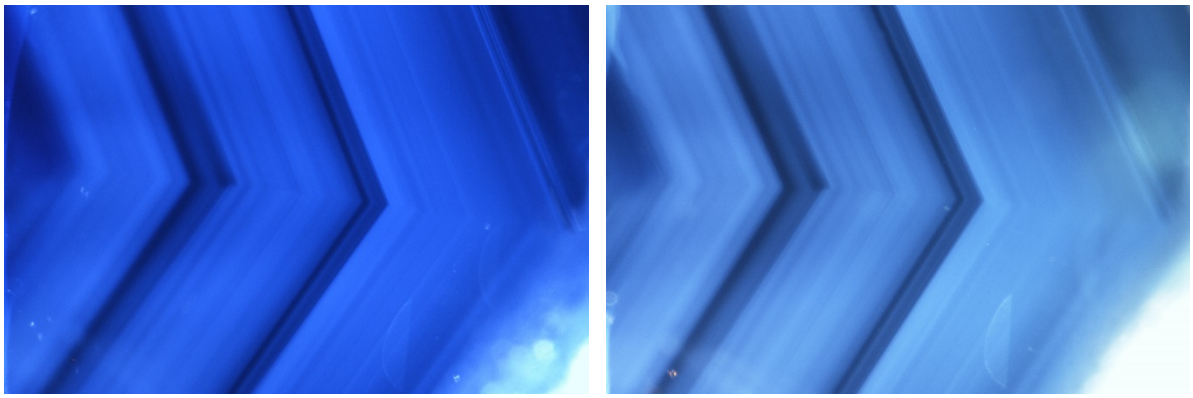


Figure 12: Sample 0950 (Australia), heated at 1050°C for 28 hours, *no signs of alteration to milky bands*, fiber-optic illumination, field of view (FOV) 2.85 mm, photomicrographs by C. Khowpong © GIA.

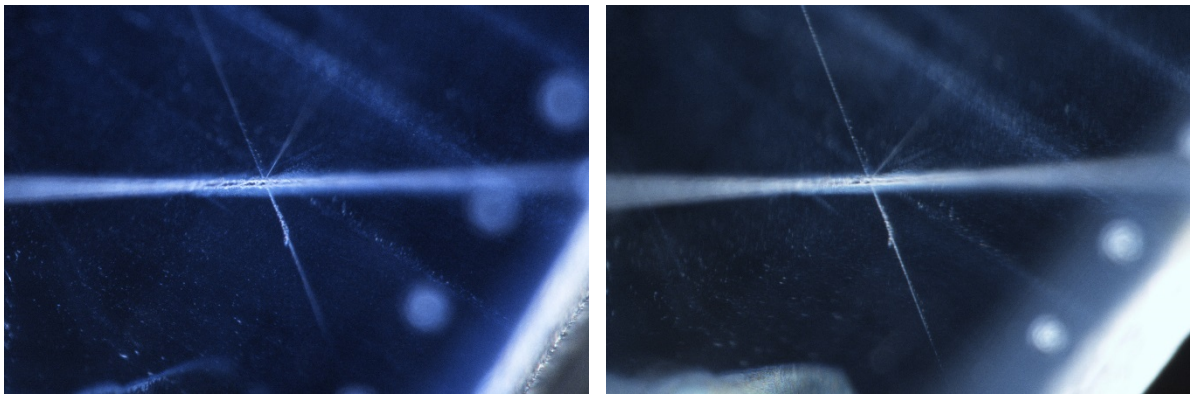


Figure 13: Sample 6543 (Cambodia), heated at 1050°C for 28 hours, *no signs of alteration to intersecting growth tubes*, darkfield illumination, FOV 1.20 mm, photomicrographs by C. Khowpong © GIA.

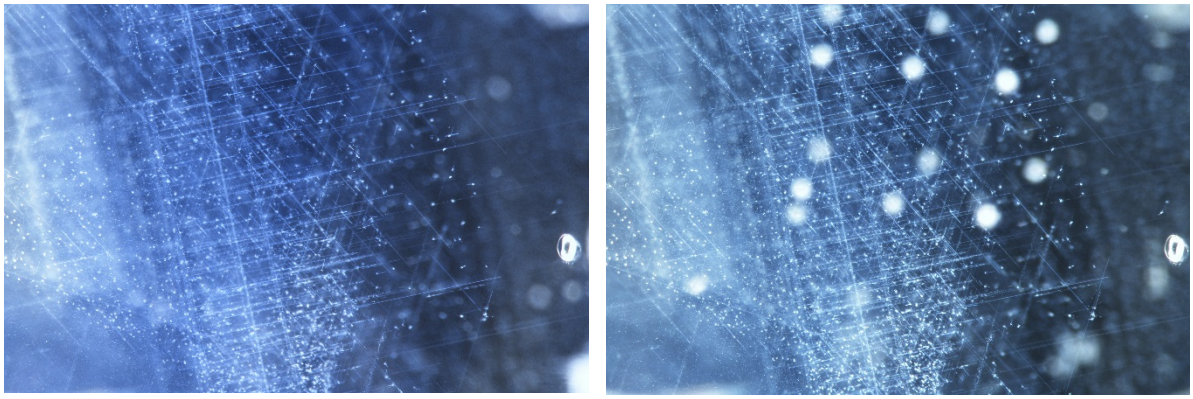


Figure 14: Sample 6545 (Thailand), heated at 1050°C for 28 hours, *no signs of alteration to needles and particles*, darkfield illumination, FOV 2.85 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating***

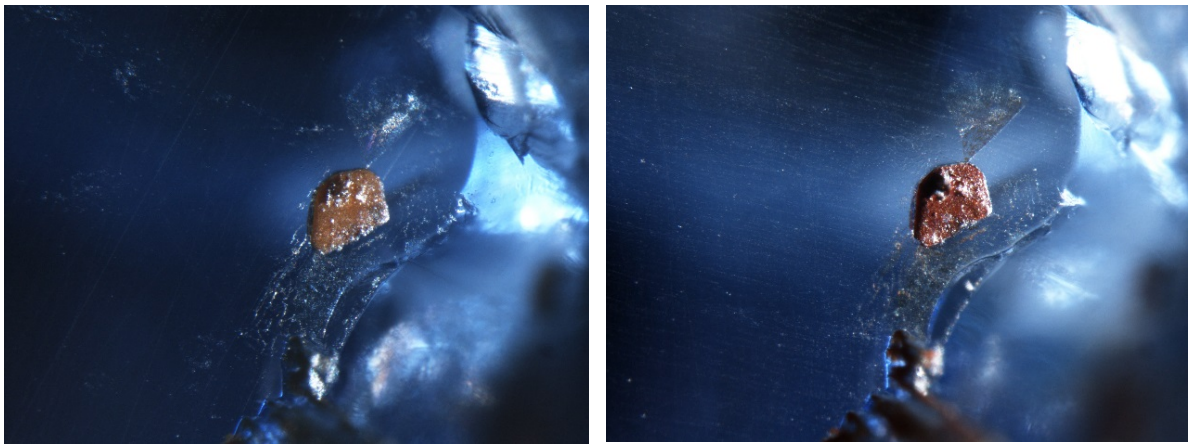


Figure 15: Sample 0896 (Australia), heated at 700°C for 28 hours, *the orange stain on solid inclusion changed to brownish red*, fiber-optic illumination, FOV 1.30 mm, photomicrographs by C. Khowpong © GIA.

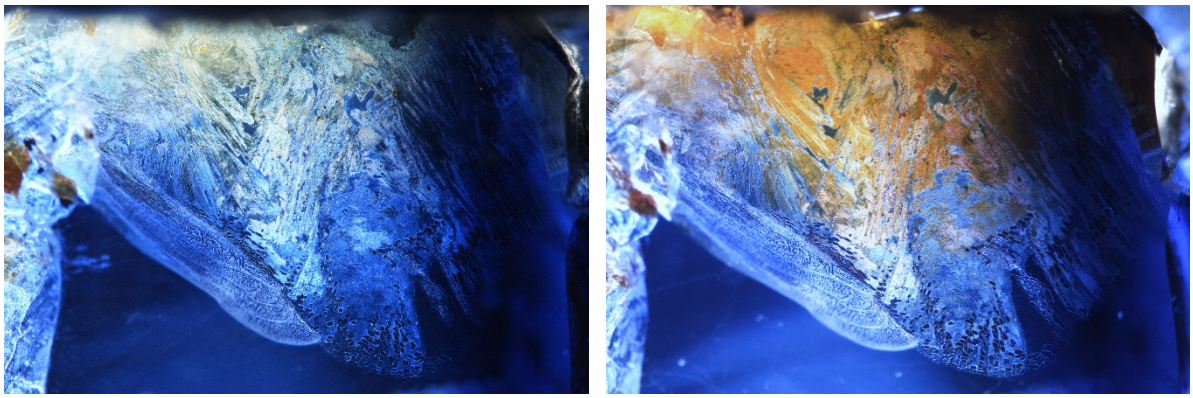


Figure 16: Sample 8102 (Cambodia), heated at 700°C for 28 hours, *no signs of alteration to the fingerprint pattern but the yellow stain changed to orange*, darkfield illumination, FOV 2.85 mm, photomicrographs by C. Khowpong © GIA.

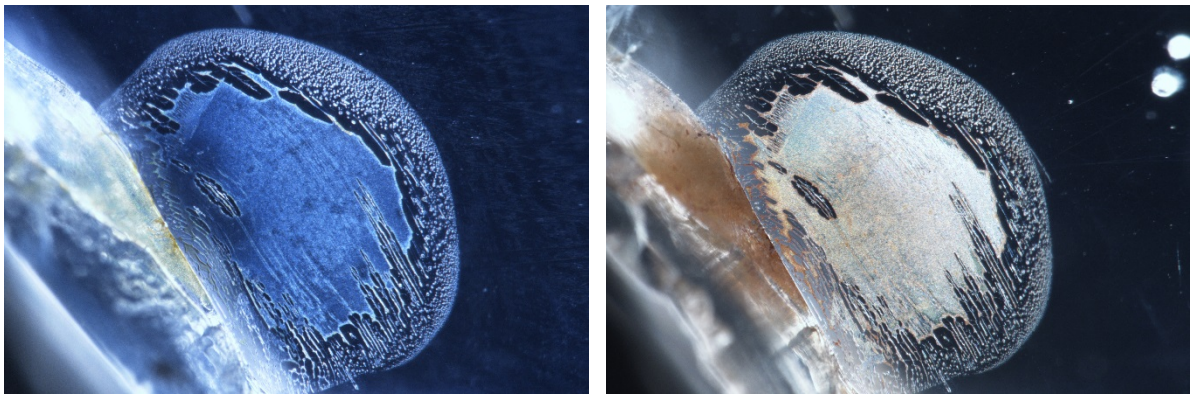


Figure 17: Sample 9458 (Thailand), heated at 1050°C for 28 hours, *no signs of alteration to fingerprint pattern, but the light yellow stain changed to brownish orange,* darkfield illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating***

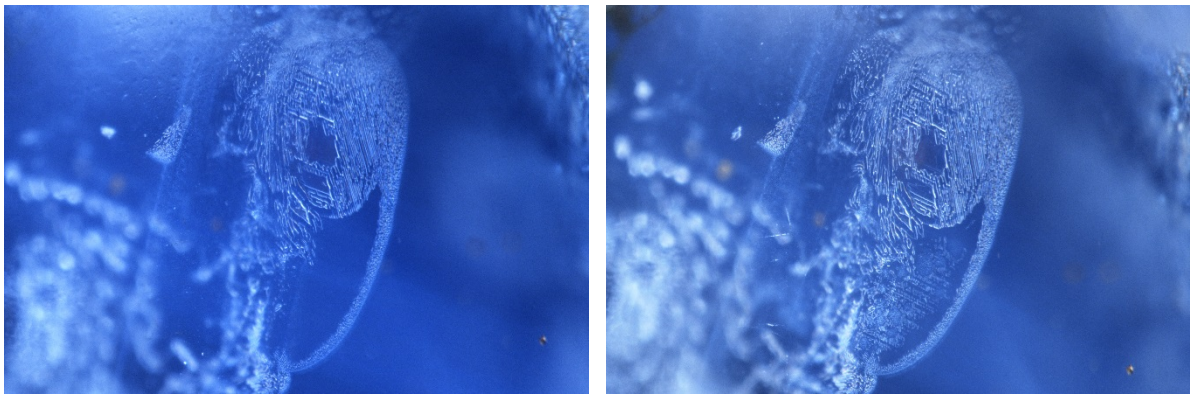


Figure 18: Sample 9902 (Cambodia), heated at 700°C for 28 hours, *some very minor alteration to an existing healed fingerprint,* darkfield illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA

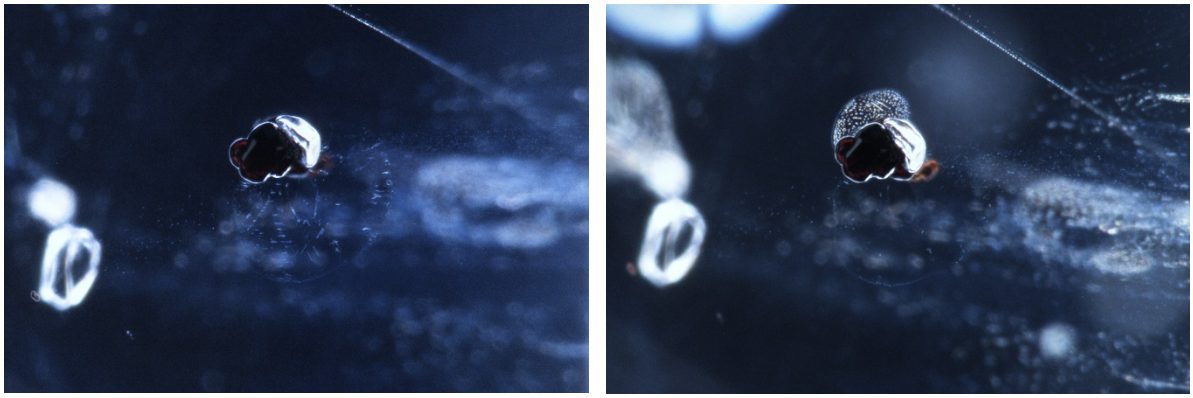


Figure 19: Sample 6543 (Cambodia), heated at 1050°C for 28 hours, *partially healed fracture developed on one side of a ferrocolumbite crystal*, darkfield illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

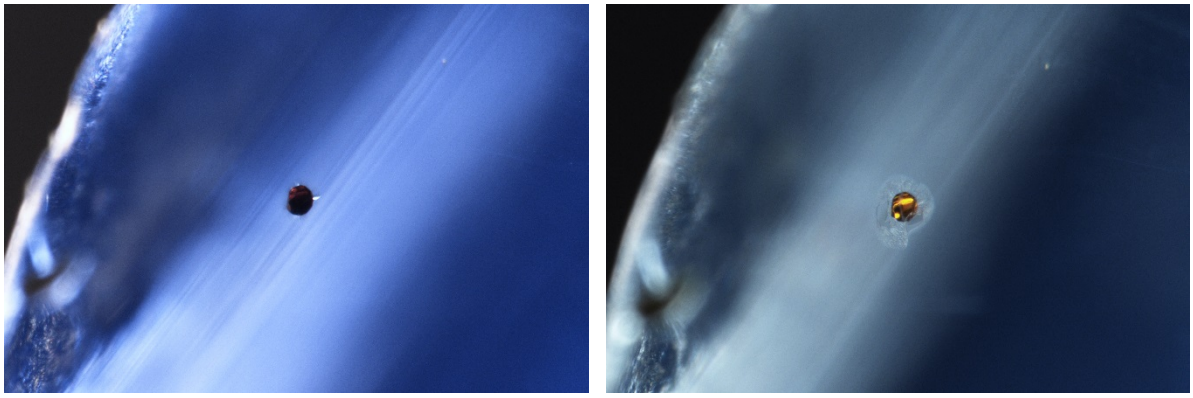


Figure 20: Sample 0950 (Australia), heated at 1050°C for 28 hours, *the dark red crystal (presumably pyrochlore) with a small tension fracture changed to an orange crystal associated with a surrounding partially healed fracture*, darkfield illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating***

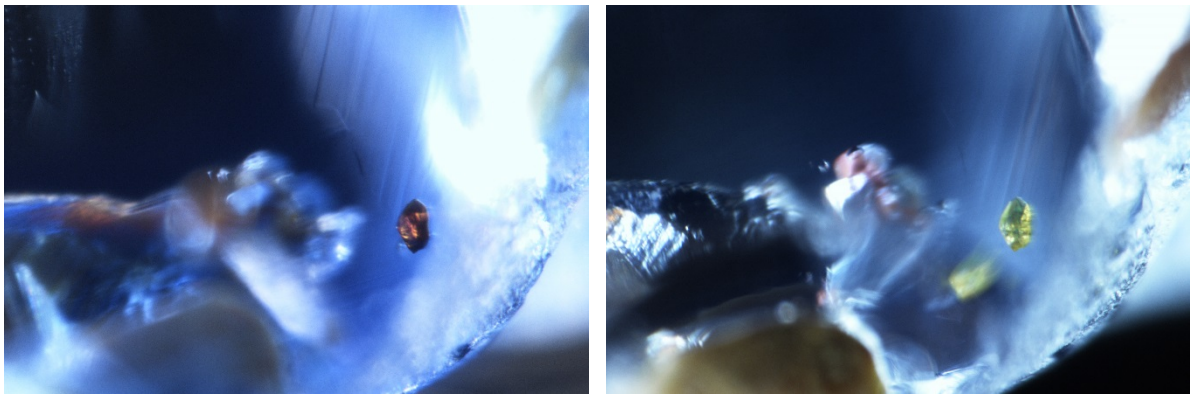


Figure 21: Sample 9489 (Nigeria), heated at 1050°C for 28 hours, *the color of an unidentified red crystal changed to yellow*, fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

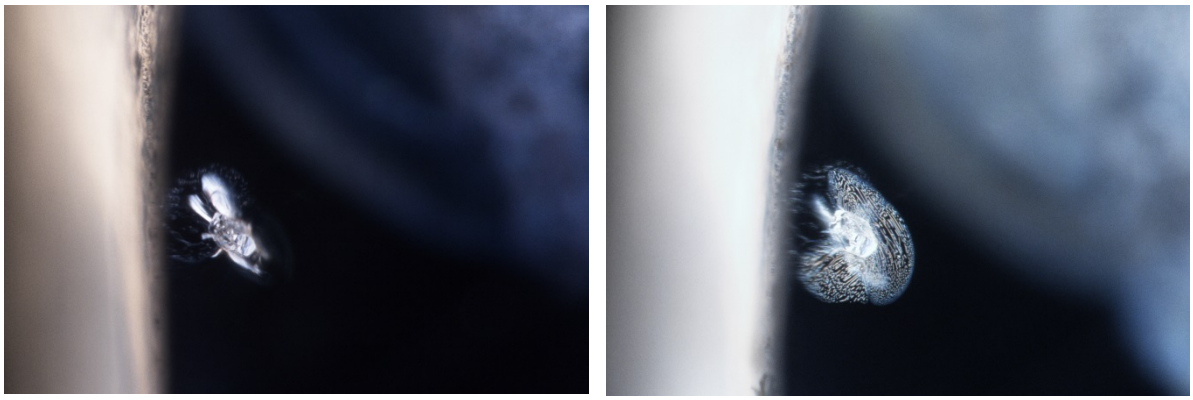


Figure 22: Sample 6543 (Cambodia), heated at 1050°C for 28 hours, *partially healed fracture developed on an unidentified colorless crystal*, darkfield illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

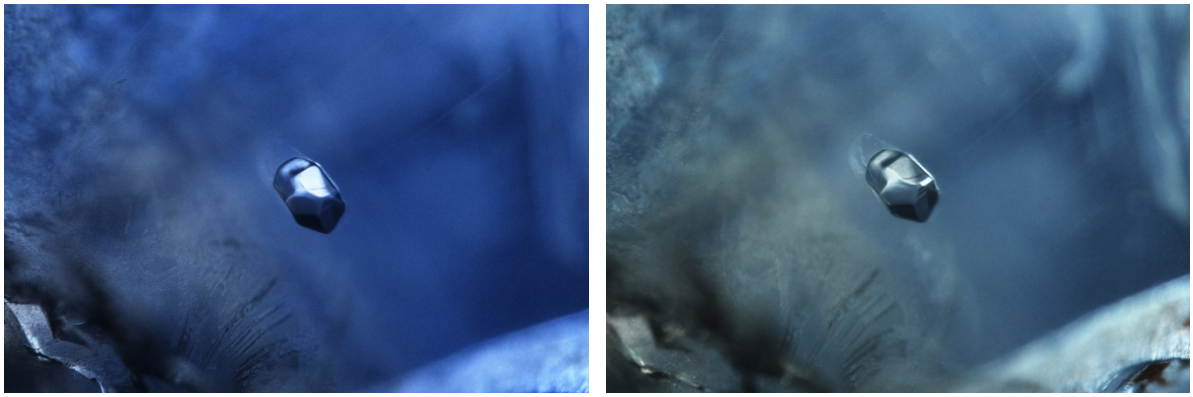


Figure 23: Sample 9310 (Thailand), heated at 1050 °C for 28 hours, *no signs of alteration to feldspar crystal*, darkfield illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating***

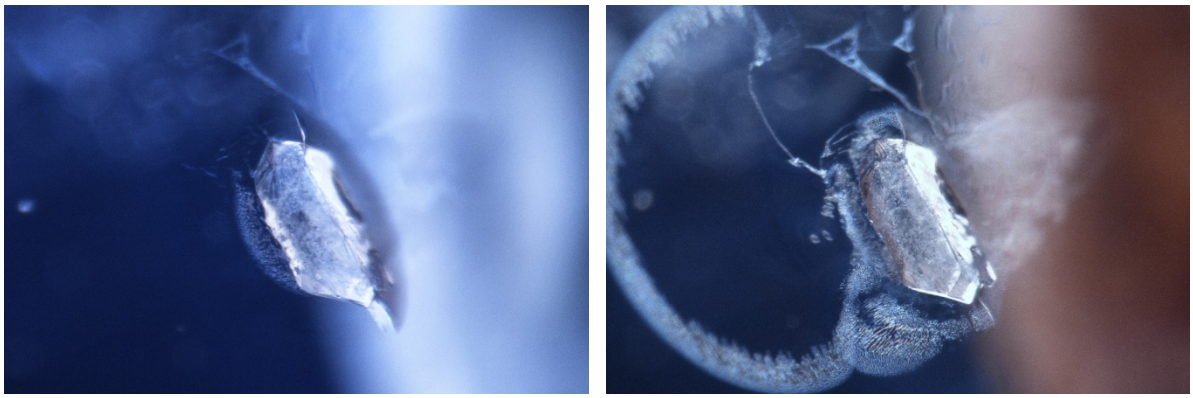


Figure 24: Sample 7132 (Cambodia), heated at 1050°C for 28 hours, *no alteration to zircon crystal but partially healed fracture developed around the crystal*, darkfield illumination, FOV 1.20 mm, photomicrographs by C. Khowpong © GIA.

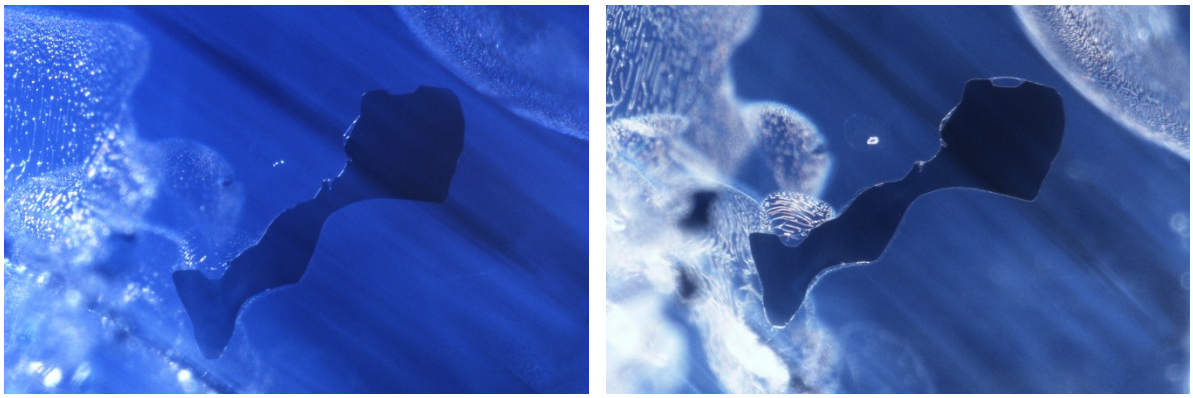


Figure 25: Sample 4246 (Australia), heated at 1050°C for 28 hours, *no signs of alteration to molybdenite platelet*, darkfield illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

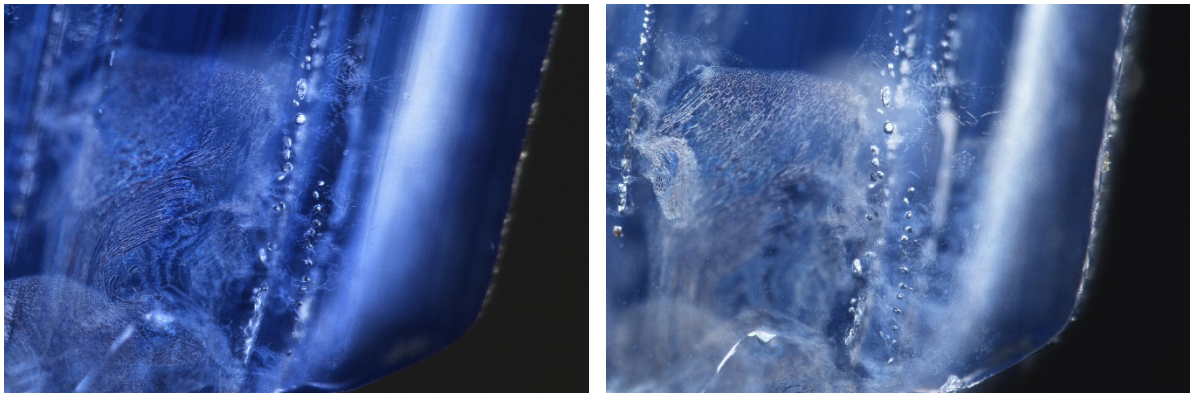


Figure 26: Sample 4246 (Australia), heated at 1050°C for 28 hours, *no alteration to row of nepheline crystals*, darkfield illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating***

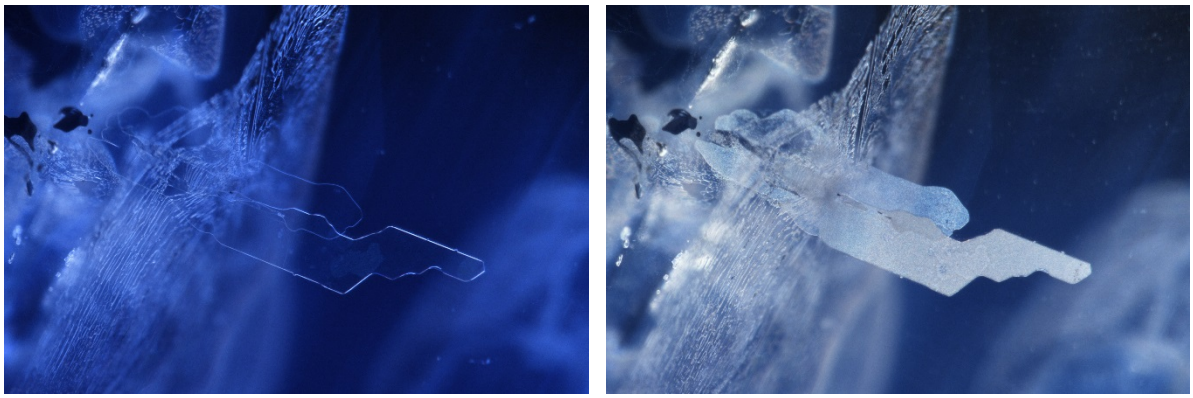


Figure 27: Sample 4246 (Australia), heated at 1050°C for 28 hours, *transparent fluid inclusion altered to an opaque frosty white form,* darkfield illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

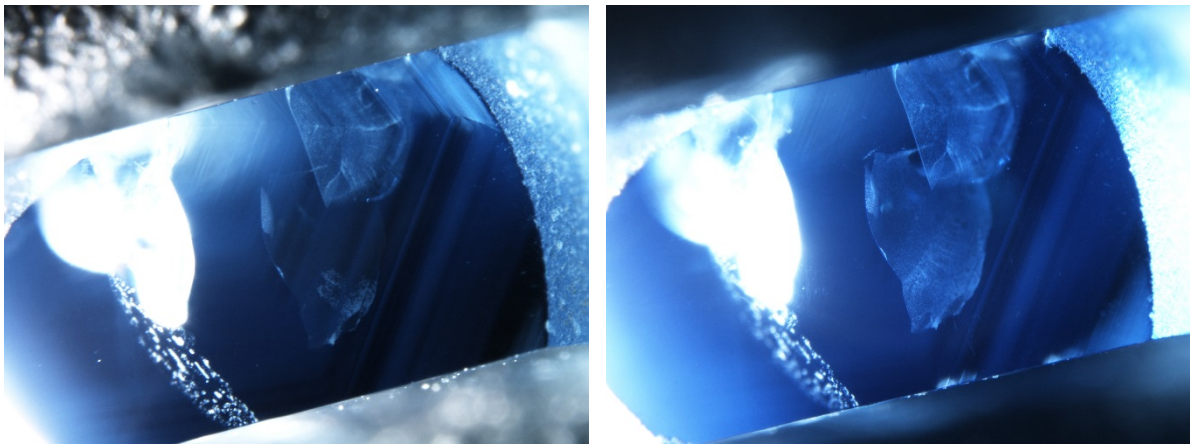


Figure 28: Sample 0620 (Australia), heated at 700°C for 28 hours, *liquid along fractures dried out and fractures look more whitish after heating*, fiber-optic illumination, FOV 2.70 mm, photomicrographs by C. Khowpong © GIA.

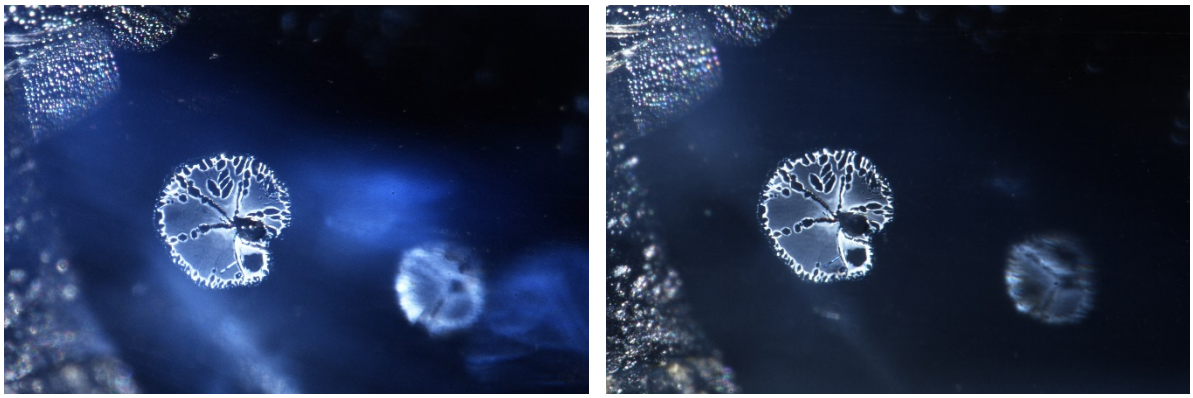


Figure 29: Sample 9424 (Australia), heated at 1050°C for 28 hours, *no signs of alteration to feldspar crystal and thin film,* fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating***

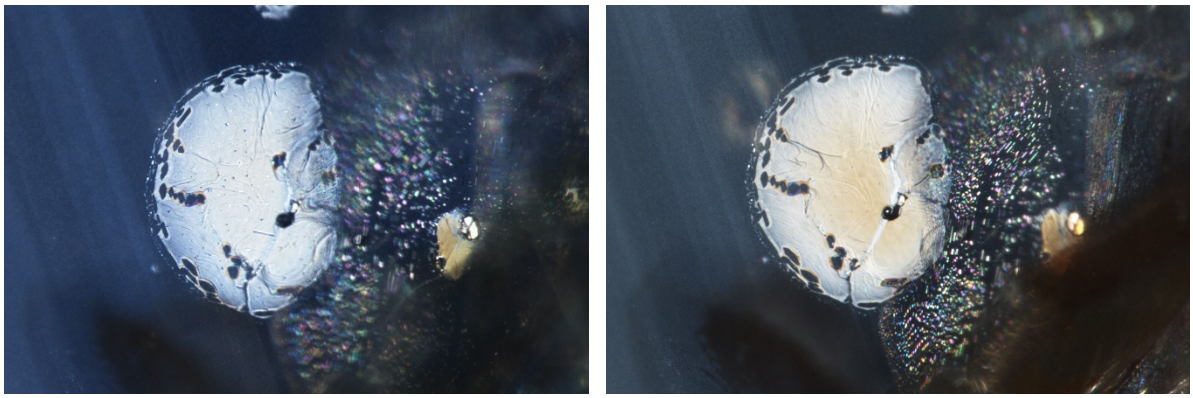


Figure 30: Sample 4780 (Nigeria), heated at 1050°C for 28 hours, *thin films look more glassy*, fiber-optic illumination, FOV 1.20 mm, photomicrographs by C. Khowpong © GIA.

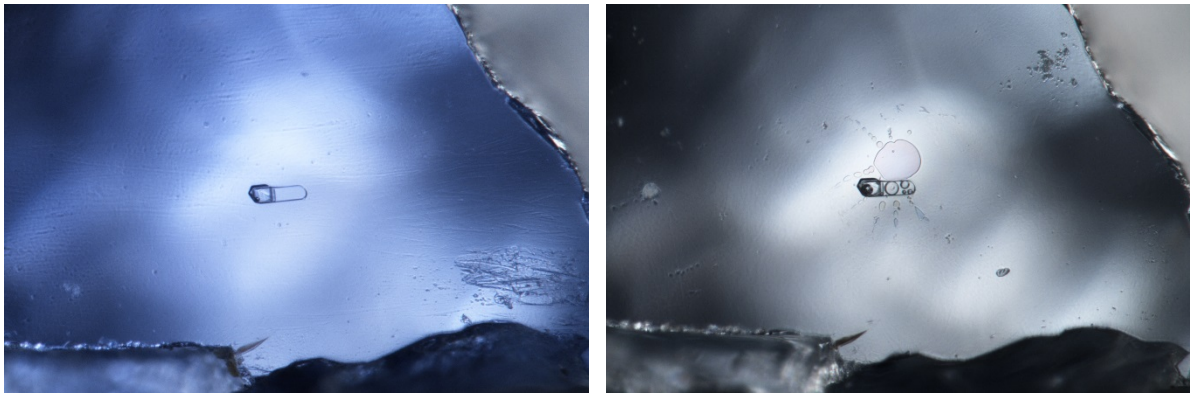


Figure 31: Sample 9458 (Thailand), heated at 1050°C for 28 hours, *gas bubbles trapped inside two-phase inclusion and alteration to thin film*, darkfield illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

Fluorescence: Unheated blue sapphires from basalt-related deposits are generally inert under short-wave UV radiation, however, one Australian blue sapphire exhibited very weak chalky fluorescence before heating (Table 1). Post treatment, most of the samples showed the same reactions as they showed prior to heating. Only two samples from Cambodia displayed very weak chalky green fluorescence after heating at 1050°C for 28 hours. The chalky fluorescence sometimes seen after heat treatment is related to aluminum vacancies associated with free Ti^{4+} created when rutile silk dissolves into the corundum lattice (Emmett *et al*, 2017).

Table 1: Fluorescence reactions of the samples before and after heat treatment at different temperatures for 28 hours.

Origin	No. of samples	Heating temperature (°C)	Fluorescence reaction under short-wave UV radiation	
			Before heating	After heating for 28 hours
Australia	5	700	Inert (4) Very weak chalky (1)	Inert (4) Very weak chalky (1)
Cambodia	5		Inert (5)	Inert (5)
Thailand	5		Inert (5)	Inert (5)
Australia	3	900	Inert (3)	Inert (3)
Cambodia	3		Inert (3)	Inert (3)
Thailand	3		Inert (3)	Inert (3)
Australia	6	1050	Inert (6)	Inert (6)
Cambodia	6		Inert (6)	Inert (4) **Very weak chalky (2)**
Thailand	6		Inert (6)	Inert (6)
Nigeria	4		Inert (6)	Inert (6)

FTIR spectroscopy: As mentioned previously, unheated basalt-related blue sapphires often display the characteristic 3309 cm^{-1} series of peaks in FTIR. Typically, the 3309 cm^{-1} peak is the strongest, and the intensities of 3232 and 3186 cm^{-1} are much lower (*e.g.* unheated spectrum in Figure 32). After heating at 700 and 900°C for 1.75 hours, the intensities of the 3309 cm^{-1} peak decreased and those of 3232 cm^{-1} increased. A slight change in peak intensities was observed with increased heating durations (Figure 32, Figure 34, Figure 36, Figure 37). However, there are some unheated basalt-related blue sapphires showing the 3309 cm^{-1} series with a relatively high 3232 cm^{-1} peak. Their spectra changed in a reverse trend after treatment (*e.g.* unheated spectrum in Figure 33). Samples that initially showed comparable intensities of 3309 and 3232 cm^{-1} peaks before treatment exhibited an increase in the 3309 cm^{-1} peak and a decrease in the 3232 cm^{-1} post treatment, and a slight change in 3309 and 3232 cm^{-1} with increasing heating durations (Figure 33, Figure 35). The change in the intensities of FTIR features after heating at 1050°C showed a slightly different trend with increased durations. After heating at 1050°C for 1.75 hours, a less intense 3309 cm^{-1} and a more intense 3232 cm^{-1} of almost comparable intensity were observed. When subsequently heated for 7 and 28 hours, the trend reversed—a more intense 3309 cm^{-1} and a less intense 3232 cm^{-1} (Figure 38, Figure 39, Figure 40, Figure 41). When heated again at longer durations, the 3309 cm^{-1} may reach its original intensity before treatment, while the 3232 cm^{-1} may be reduced to less than its original unheated intensity (Figure 39, Figure 41). The inverse intensities between 3309 and 3232 or 3186 cm^{-1} after heating correspond to a previous report by Moon and Philip (1991). It should be noted that although Thai blue sapphires are from basalt-related deposits, their FTIR spectra before treatment usually displayed a single weak 3309 cm^{-1} peak. A decrease in the intensities of the 3309 cm^{-1} peak and the development of a 3232 cm^{-1} peak after heat treatment were also recorded. However, the 3309 and 3232 cm^{-1} peak in the initial FTIR spectra sometimes disappeared after treatment at certain conditions (Figure 42).

FTIR spectra obtained from the samples in this study were shown to vary quite considerably, with the peak intensities recorded before each treatment process showing differences to those recorded at each temperature employed, and also for the durations used during the treatment at each temperature. The variable results on the effect of heat treatment to FTIR features was also reported in Sutthirat *et al.* (2006).

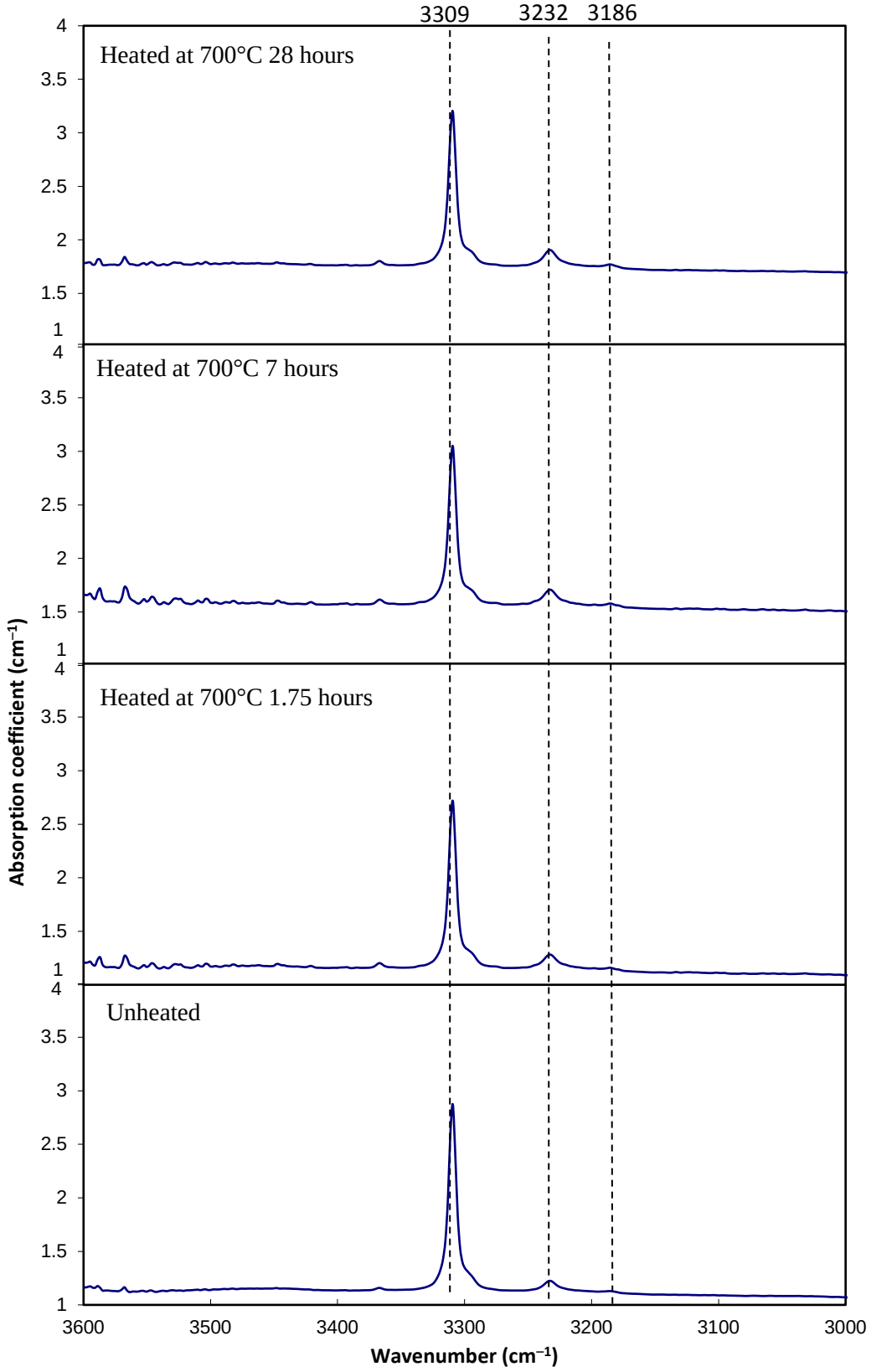


Figure 32: FTIR spectra of sample 0896 (Australia) before and after heating at 700°C for different durations.

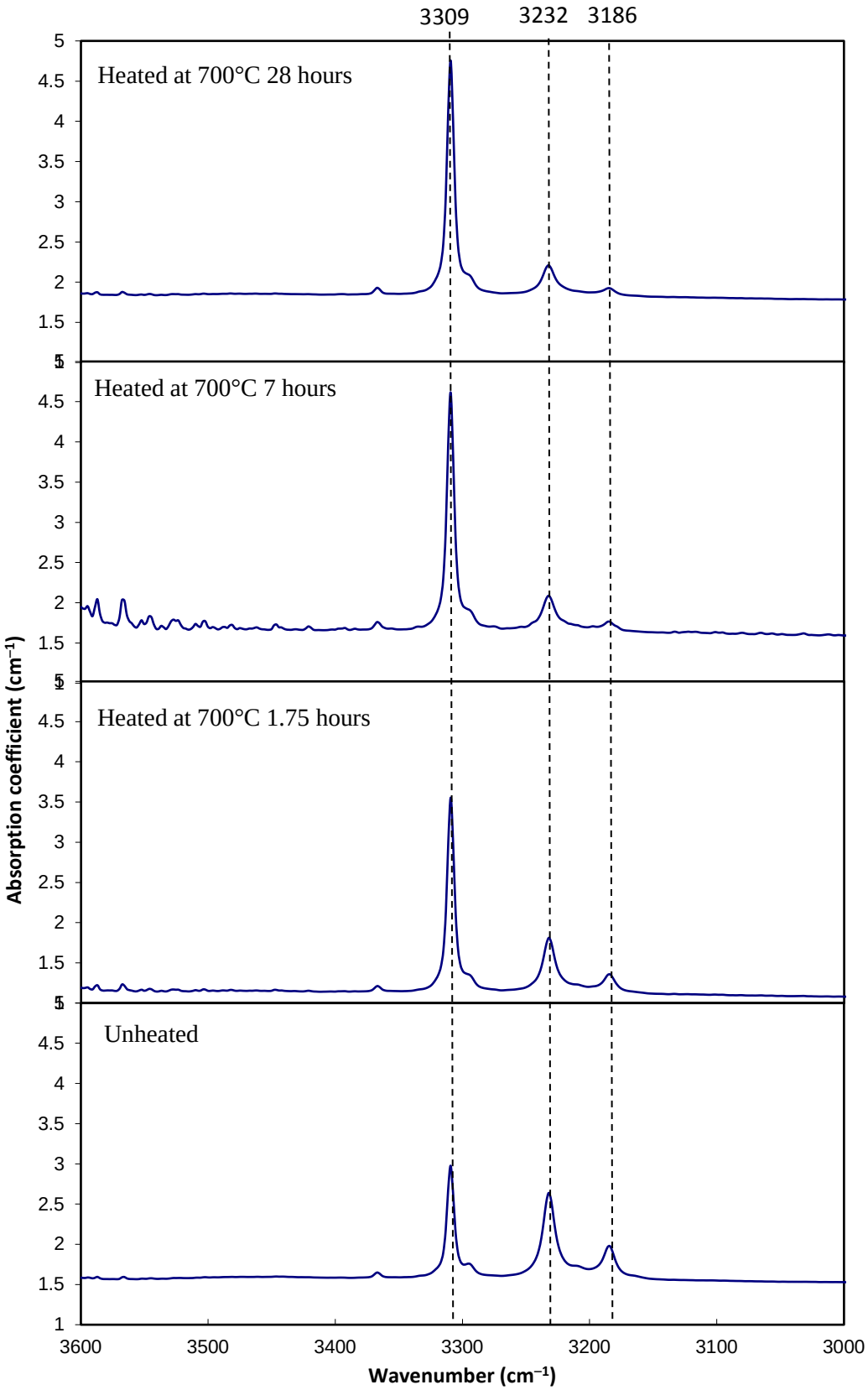


Figure 33: FTIR spectra of sample 1941 (Cambodia) before and after heating at 700°C for different durations.

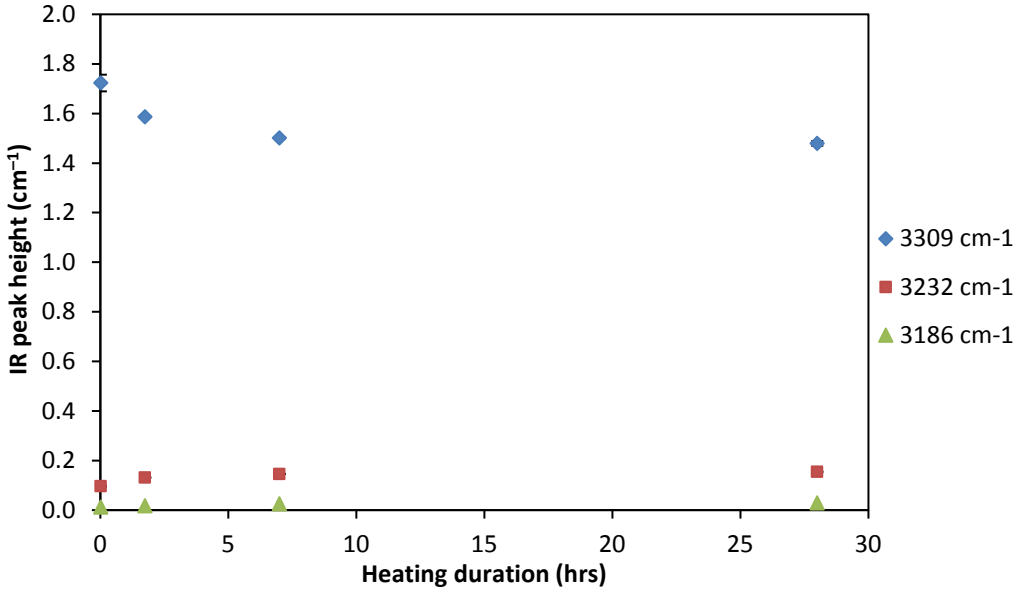


Figure 34: Plot of FTIR peak height of sample 0896 (Australia) before and after heating at 700°C for different durations from spectra in Figure 32.

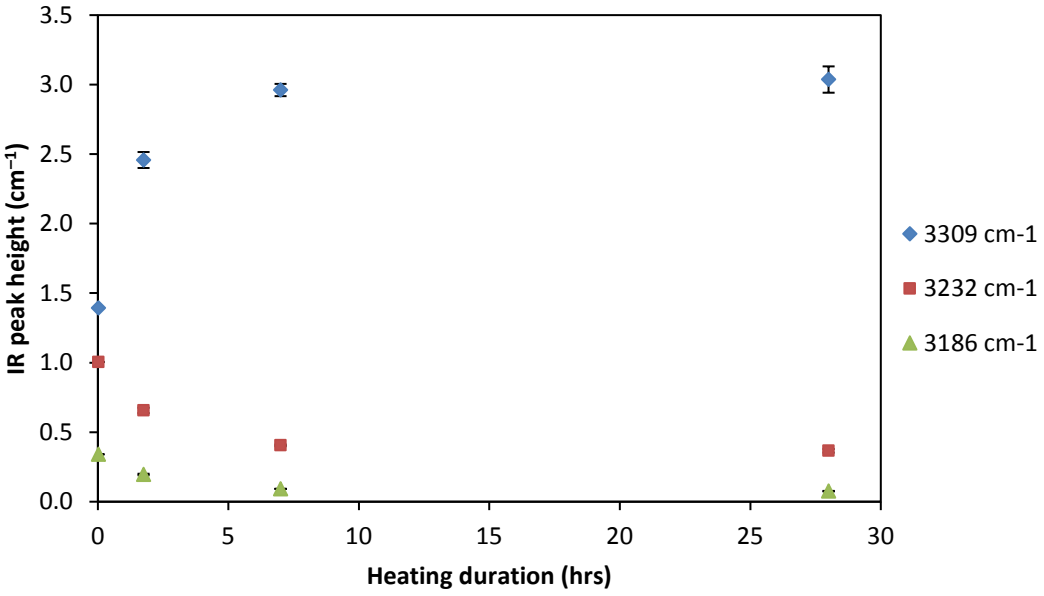


Figure 35: Plot of FTIR peak height of sample 1941 (Cambodia) before and after heating at 700°C for different durations from spectra in Figure 33.

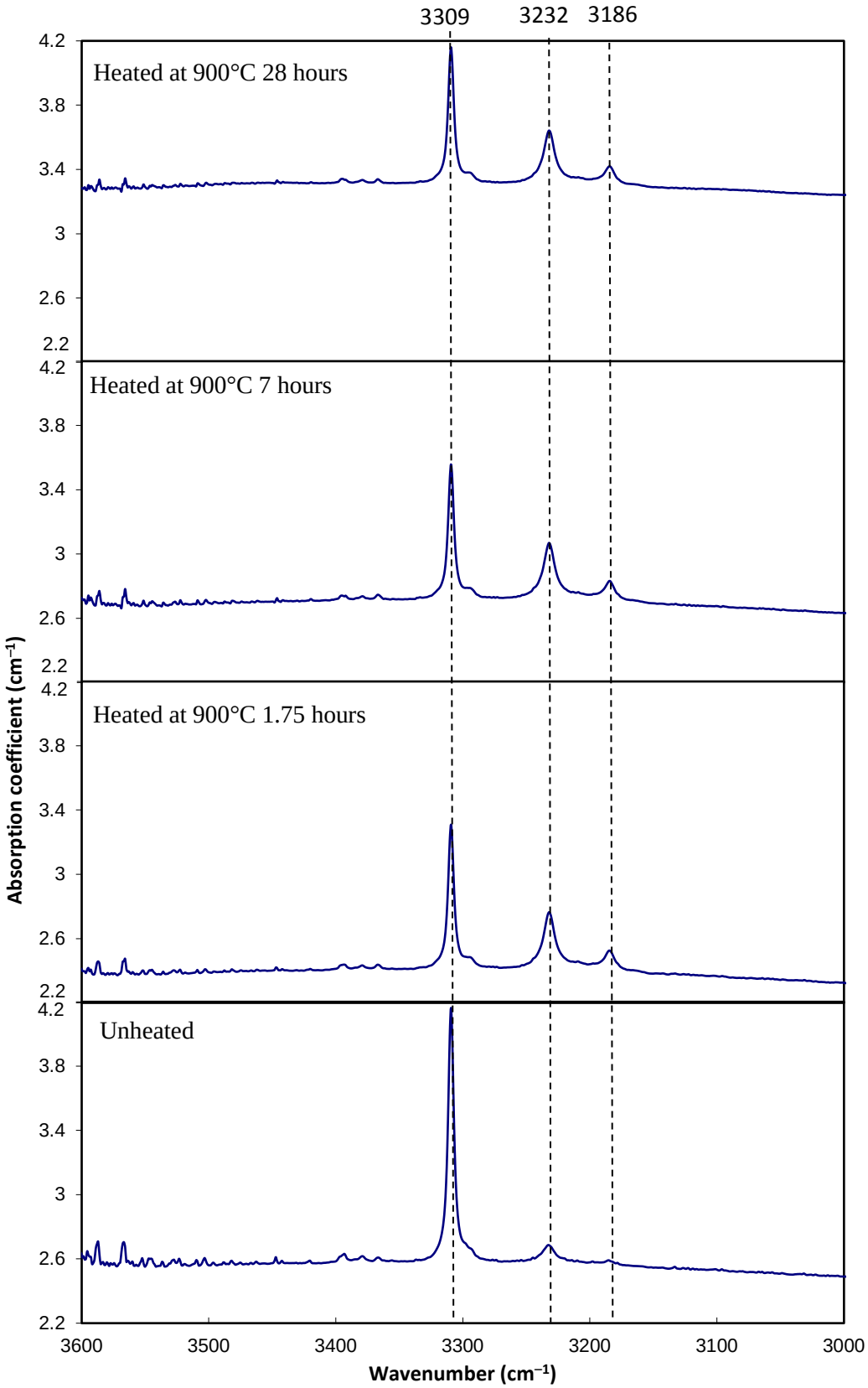


Figure 36: FTIR spectra of sample 6542 (Cambodia) before and after heating at 900°C for different durations.

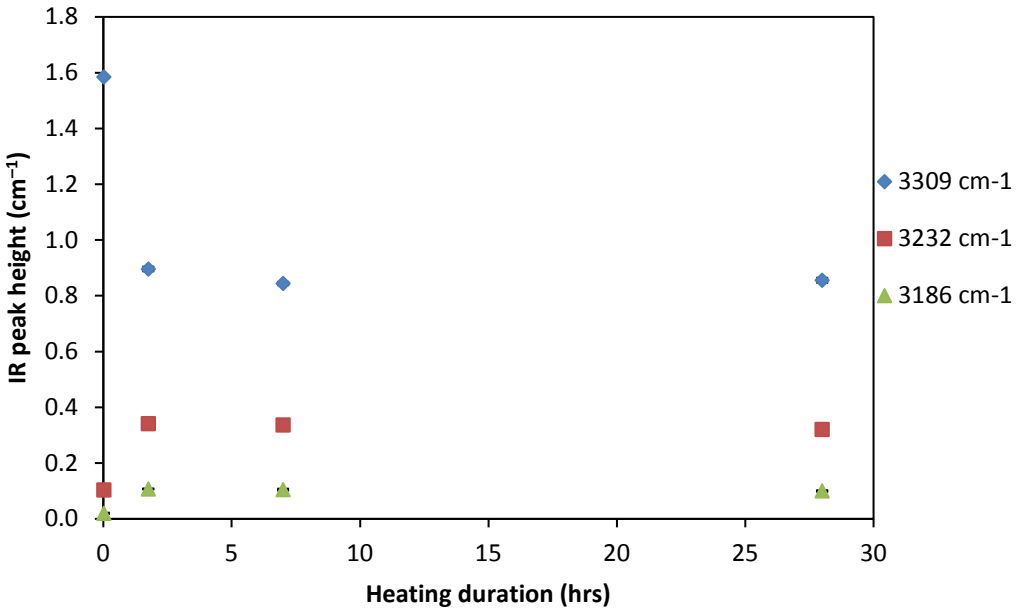


Figure 37: Plot of FTIR peak height of sample 6542 (Cambodia) before and after heating at 900°C for different durations from spectra in Figure 36.

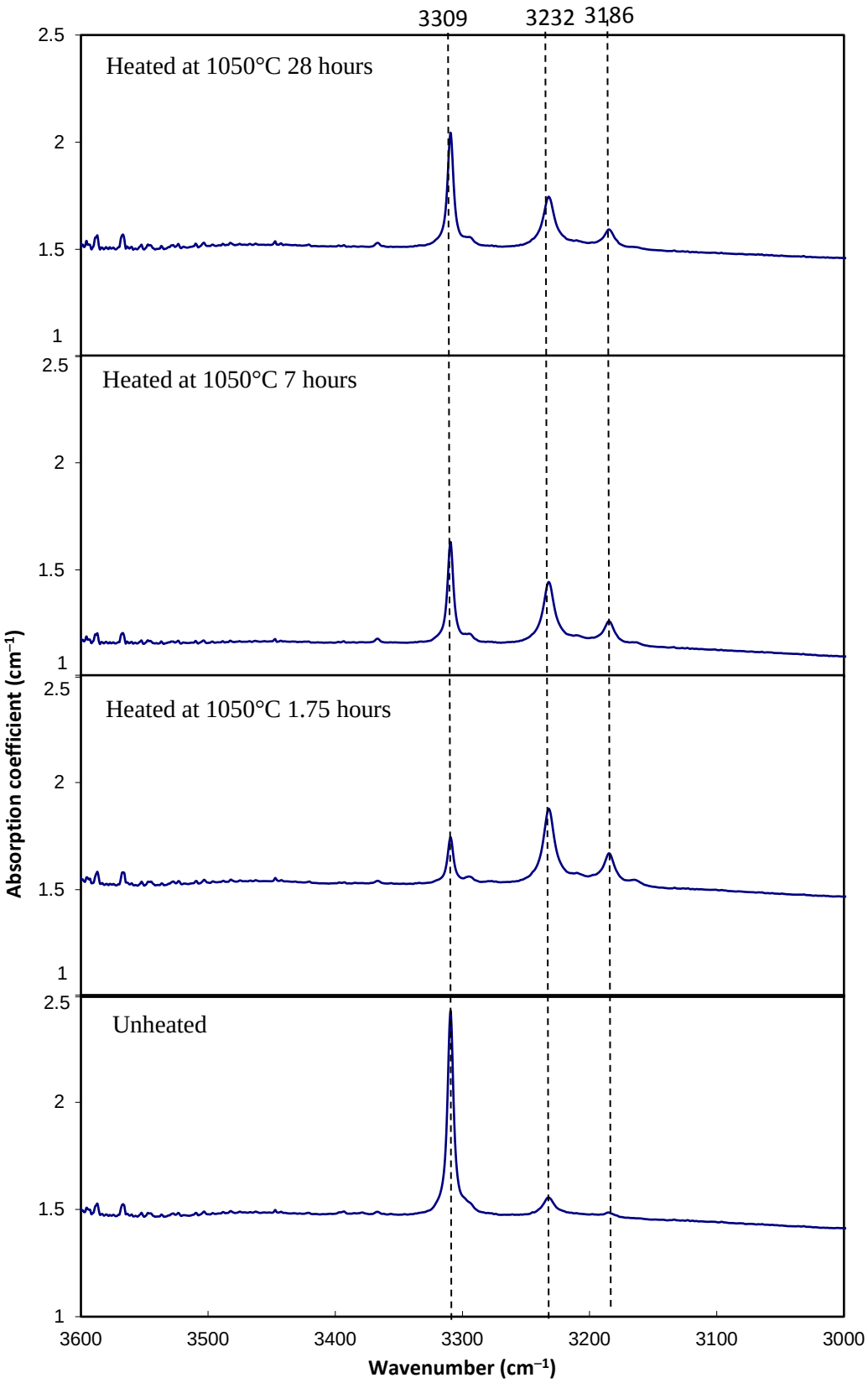


Figure 38: FTIR spectra of sample 6540 (Cambodia) before and after heating at 1050°C for different durations.

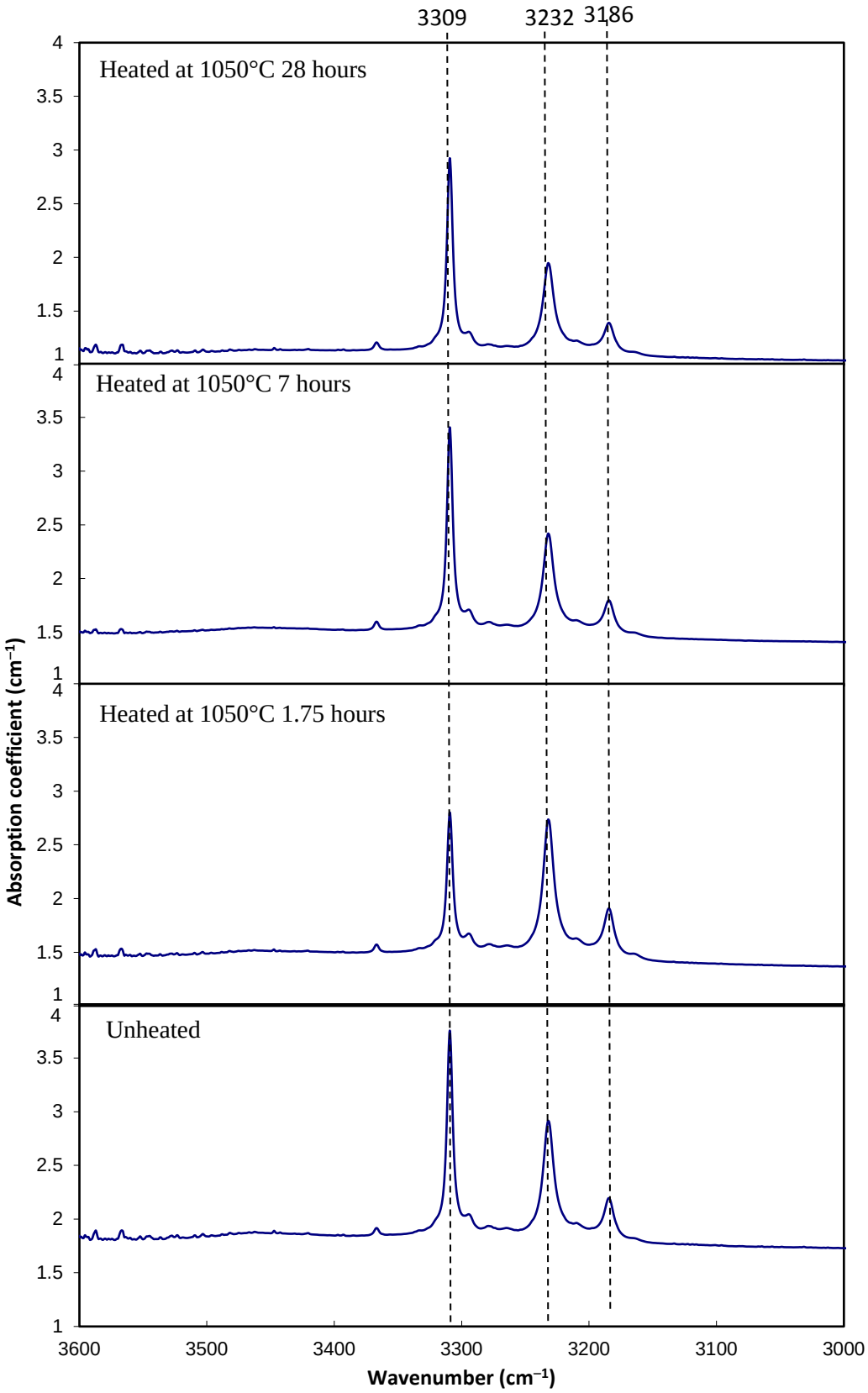


Figure 39: FTIR spectra of sample 6547 (Cambodia) before and after heating at 1050°C for different durations.

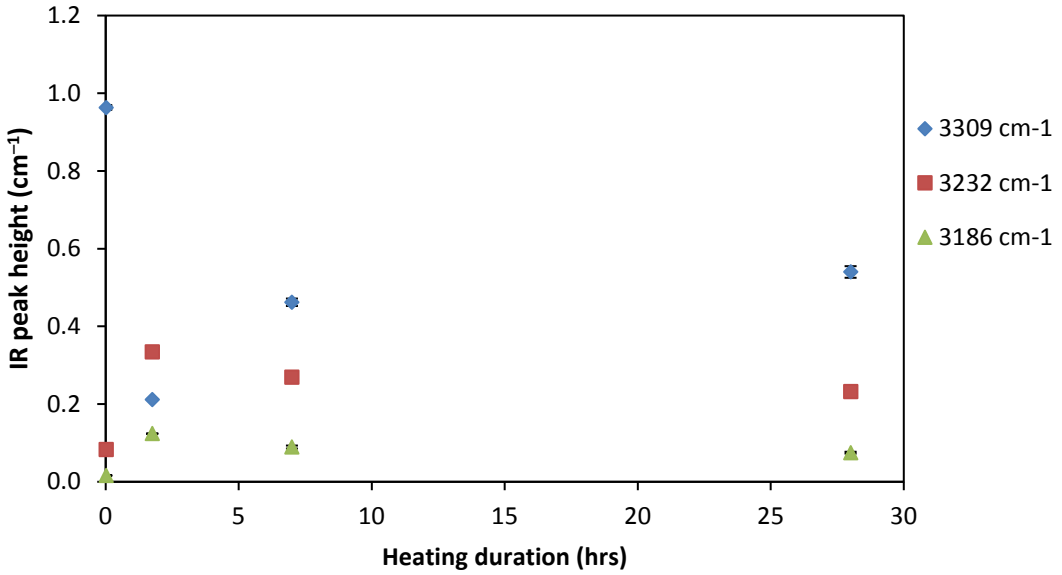


Figure 40: Plot of FTIR peak height of sample 6540 (Cambodia) before and after heating at 1050°C for different durations from spectra in Figure 38.

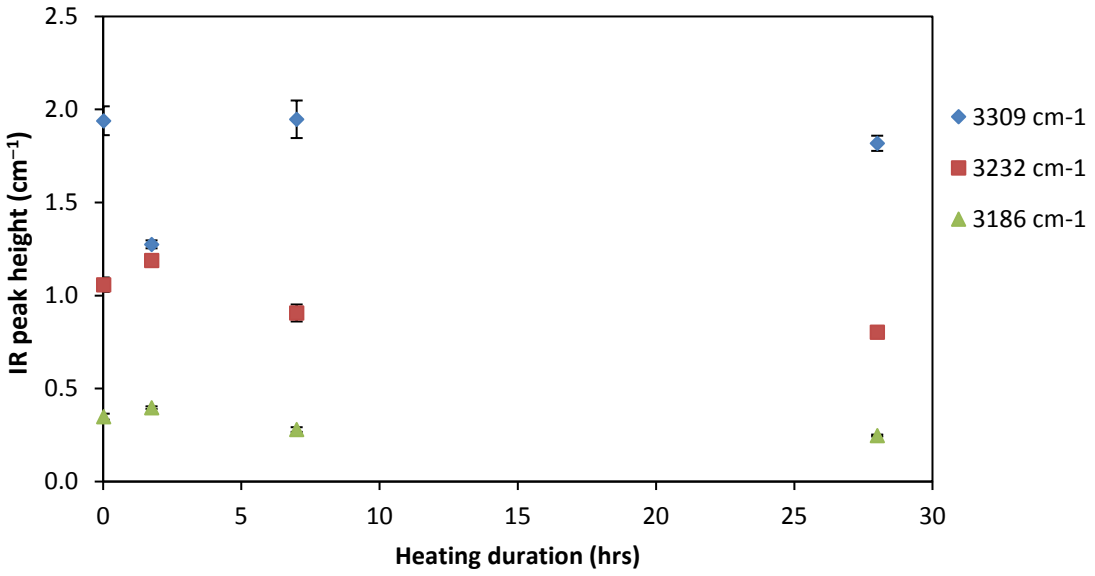


Figure 41: Plot of FTIR peak height of sample 6547 (Cambodia) before and after heating at 1050°C for different durations from spectra in Figure 39.

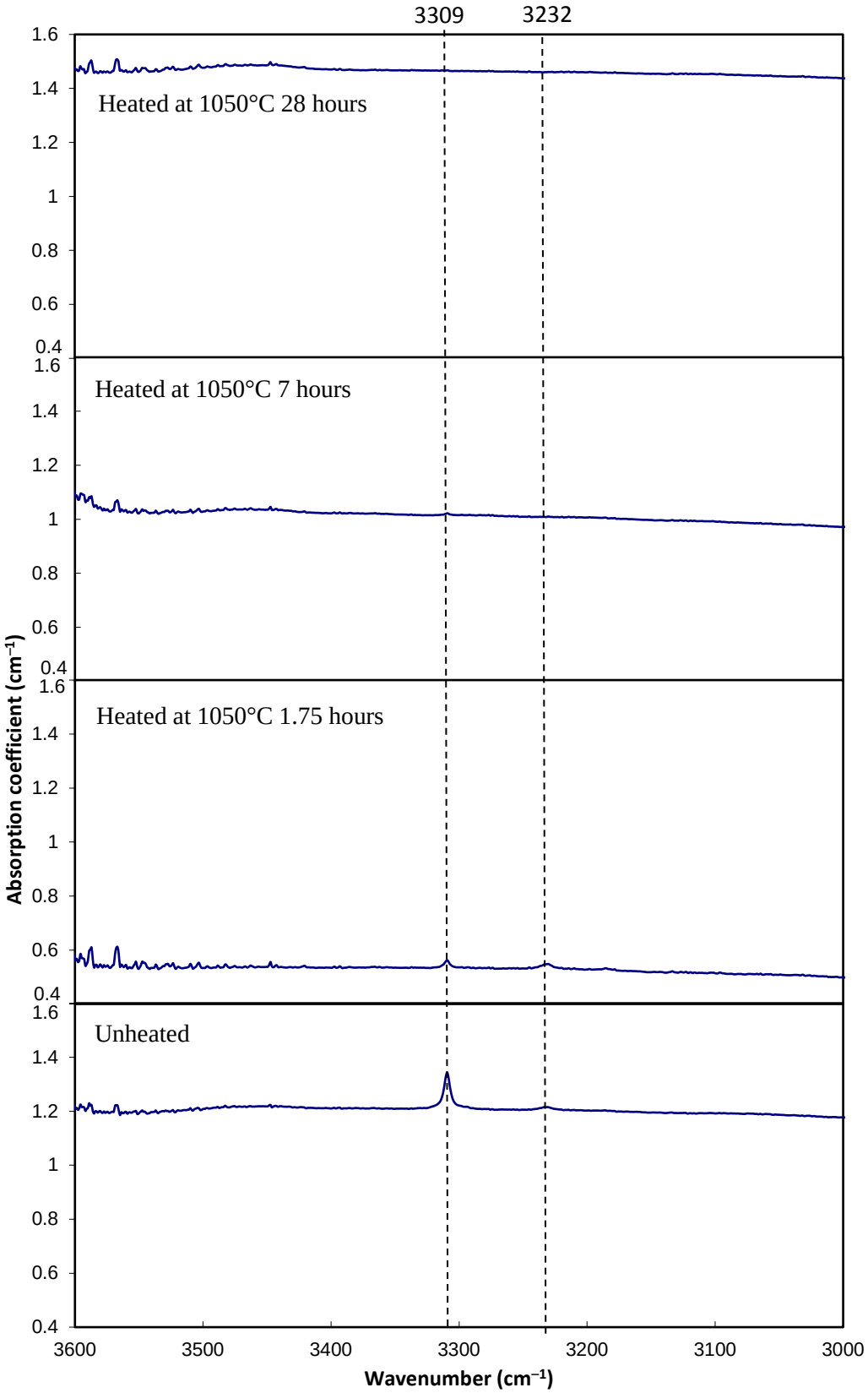


Figure 42: FTIR spectra of sample 9458 (Thailand) before and after heating at 1050°C for different durations.

UV-Vis-NIR Spectroscopy: Prior to heat treatment, UV-Vis-NIR spectra of the samples revealed an Fe^{3+} absorption peaks at 377, 388, and 450 nm, an Fe^{2+}-Ti^{4+} pair absorption band centered at 580 nm, as well as a broad band centered at around 880 nm which is typically seen in sapphires from basalt-related deposits. In the experiments, the color alteration of all samples corresponds with their UV-Vis-NIR spectra obtained. Negligible or a slight decrease in the intensities of the broad band centered at 580 nm was observed after heating at 700°C (Figure 43, Figure 47), whereas a significant reduction of that band was obtained after heating at 900 and 1050°C (Figure 45, Figure 46, Figure 49, Figure 50). The reduction of the Fe^{2+}-Ti^{4+} intervalence charge transfer band in UV-Vis-NIR spectra is related to the lightening of blue color after treatment. As shown in e-ray spectra of Figure 43, Figure 45, and Figure 46, the peak positions of the broad band in the red and near infrared region shifted to longer wavelengths after heating. In addition, the broad band at 890 nm in most of the treated Australian and Thai sapphires tended to increase in intensity, whereas the Cambodian samples showed a negligible to slight change in that band's intensity after heating (Figure 47, Figure 49, Figure 50).

The result of heat treatment also depends on the nature of corundum before heating (Themelis, 2018). In this experiment, some samples had a more intense blue color after heating at 700°C (Figure 9). Their UV-Vis-NIR spectra after treatment showed an increase of Fe^{2+}-Ti^{4+} pairs in the absorption band at 580 nm (Figure 44, Figure 48). At the same condition, treated samples that had a more intense blue color showed the 3309 cm^{-1} series with a relatively high 3232 cm^{-1} peak in their FTIR spectra (Figure 48), whereas the lighter blue samples exhibited much lower intensities of 3232 cm^{-1} than the 3309 cm^{-1} peak (Figure 47) before heating at 700°C. Since the stretching frequency/peak position of the OH group in FTIR strongly depends on its local crystallographic environment or structural arrangement, different initial FTIR spectra gave different results in color appearance after treatment. However, one sample displaying a relatively high intensity of 3232 cm^{-1} showed a reduction in blue color after heating at 1050°C for 28 hours. The results support various factors affecting the change in treated corundum.

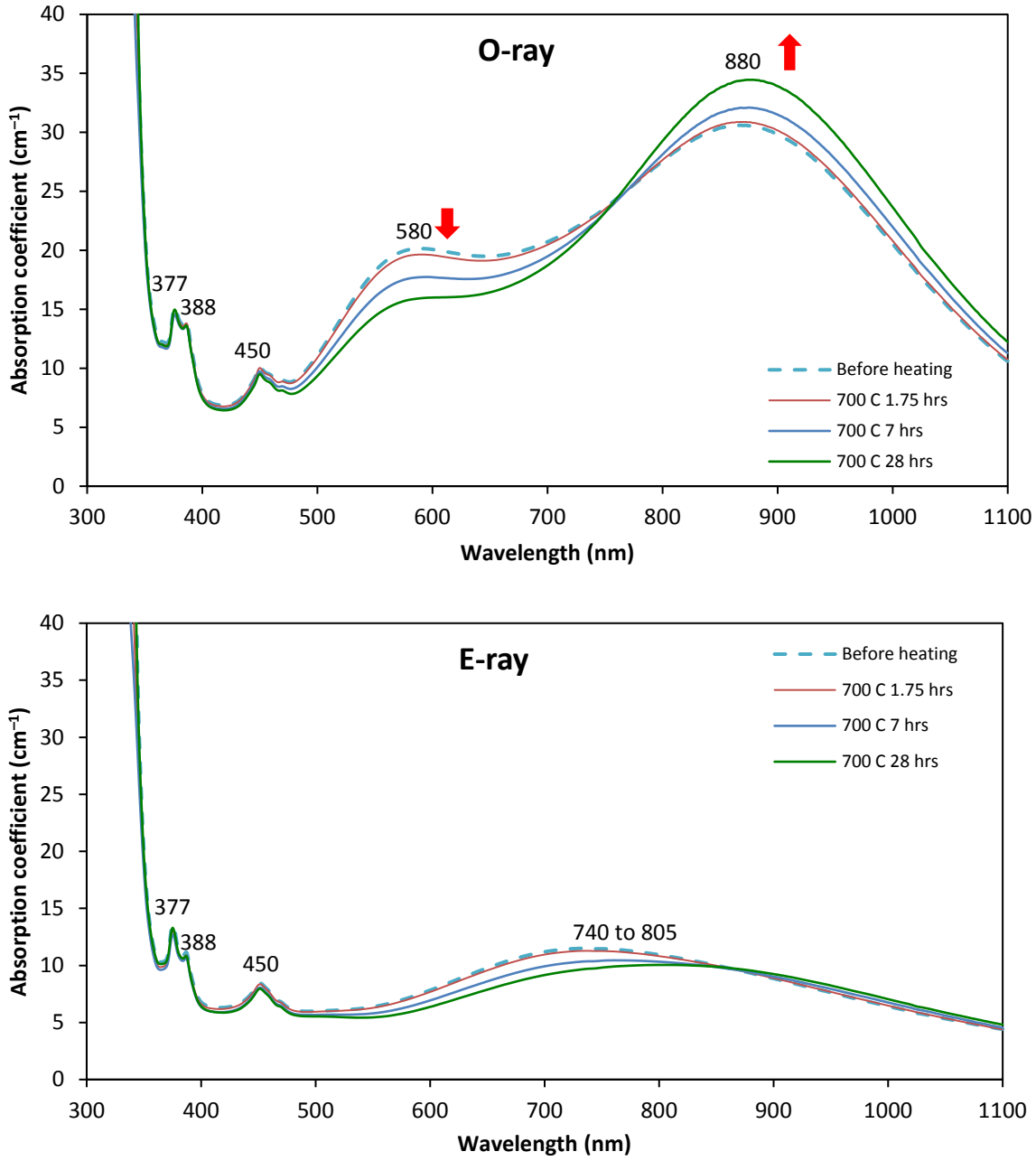


Figure 43: UV-Vis-NIR spectra of sample 4702 (Thailand) with wafer plane parallel to c-axis, before and after heating at 700°C for different durations. Optical path length 1.052 mm, α(max) 29 cm^{-1}.

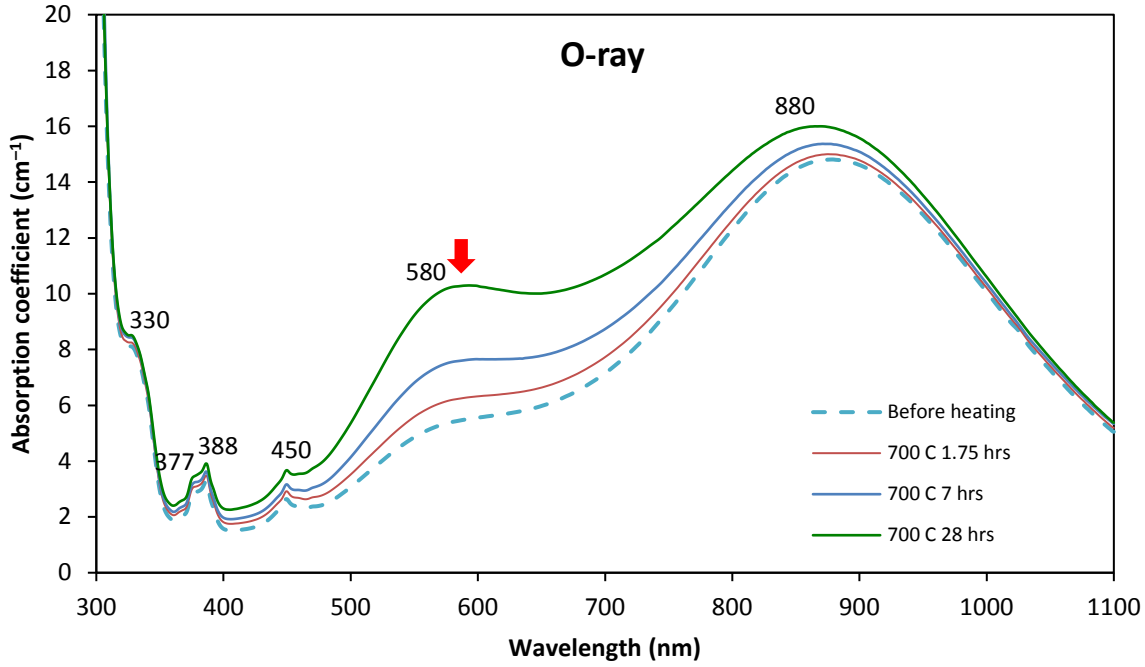


Figure 44: UV-Vis-NIR spectra of sample 1941 (Cambodia) with wafer plane perpendicular to c-axis, before and after heating at 700°C for different durations. Optical path length 1.443 mm, α(max) 21 cm^{-1}.

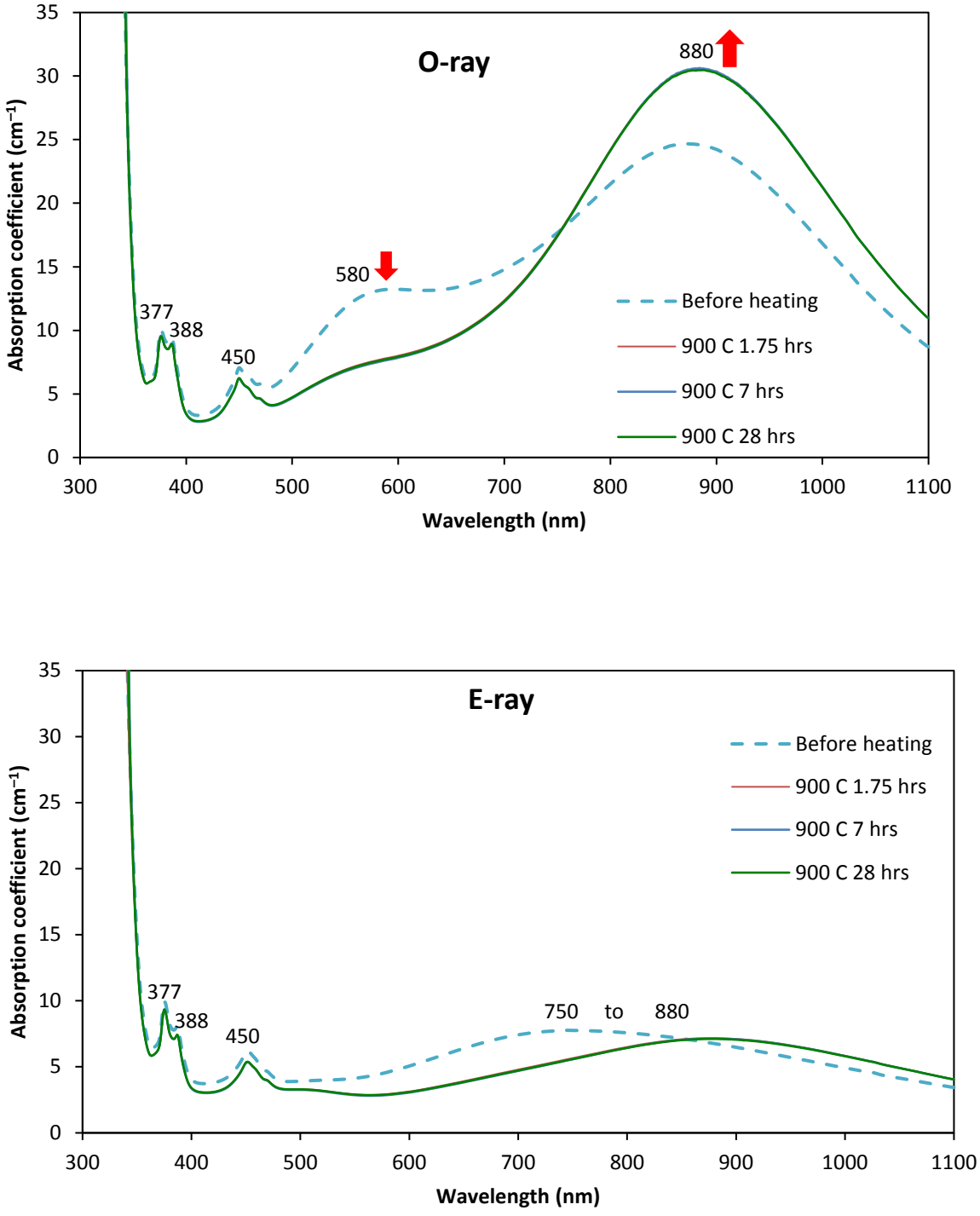


Figure 45 : UV-Vis-NIR spectra of sample 2738 (Australia) with wafer plane parallel to c-axis, before and after heating at 900°C for different durations. Optical path length 1.334 mm, α(max) 27 cm^{-1}.

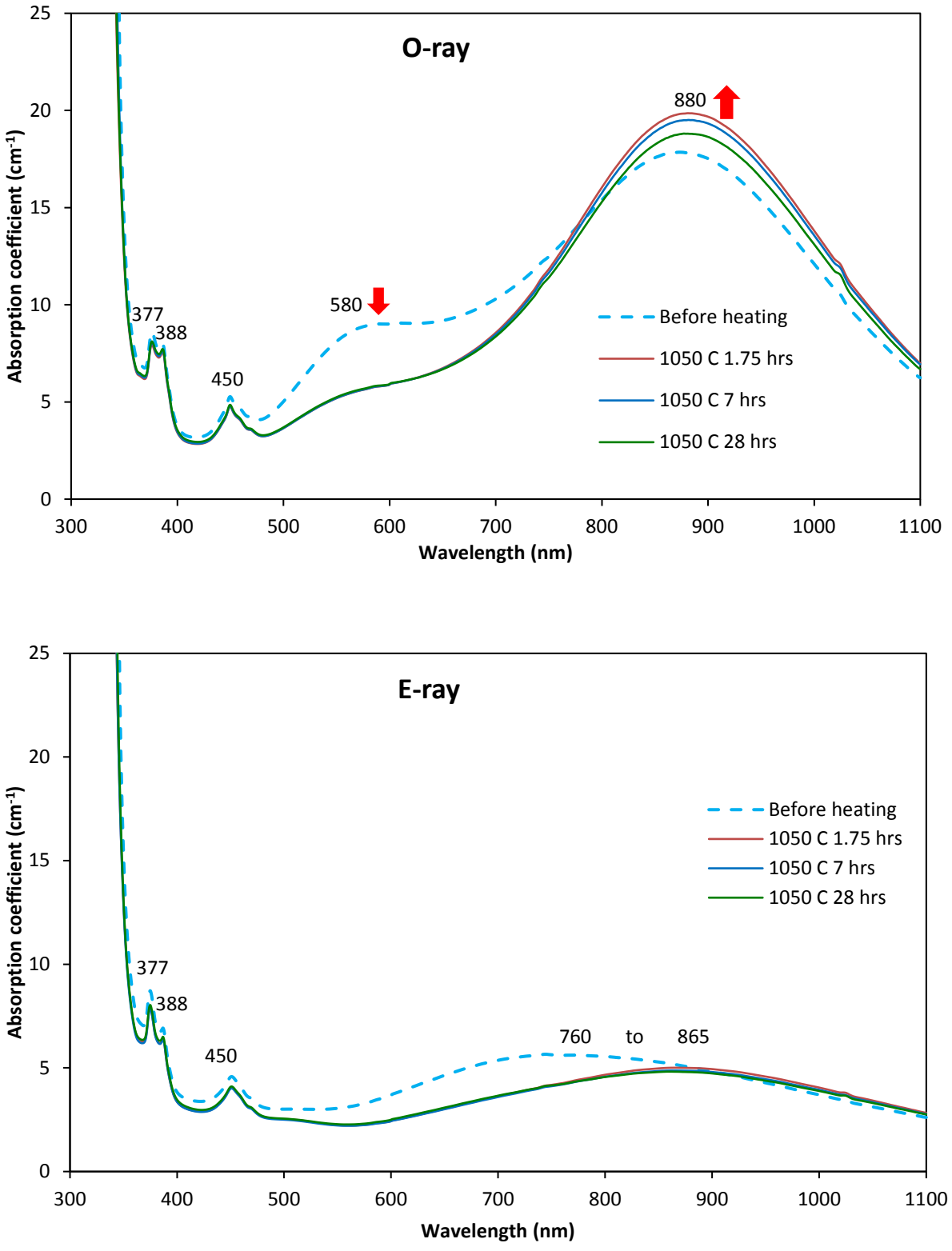


Figure 46: UV-Vis-NIR spectra of sample 0859 (Australia) with wafer plane parallel to c-axis, before and after heating at 1050°C for different durations. Optical path length 1.680 mm, α(max) 18 cm^{-1}.

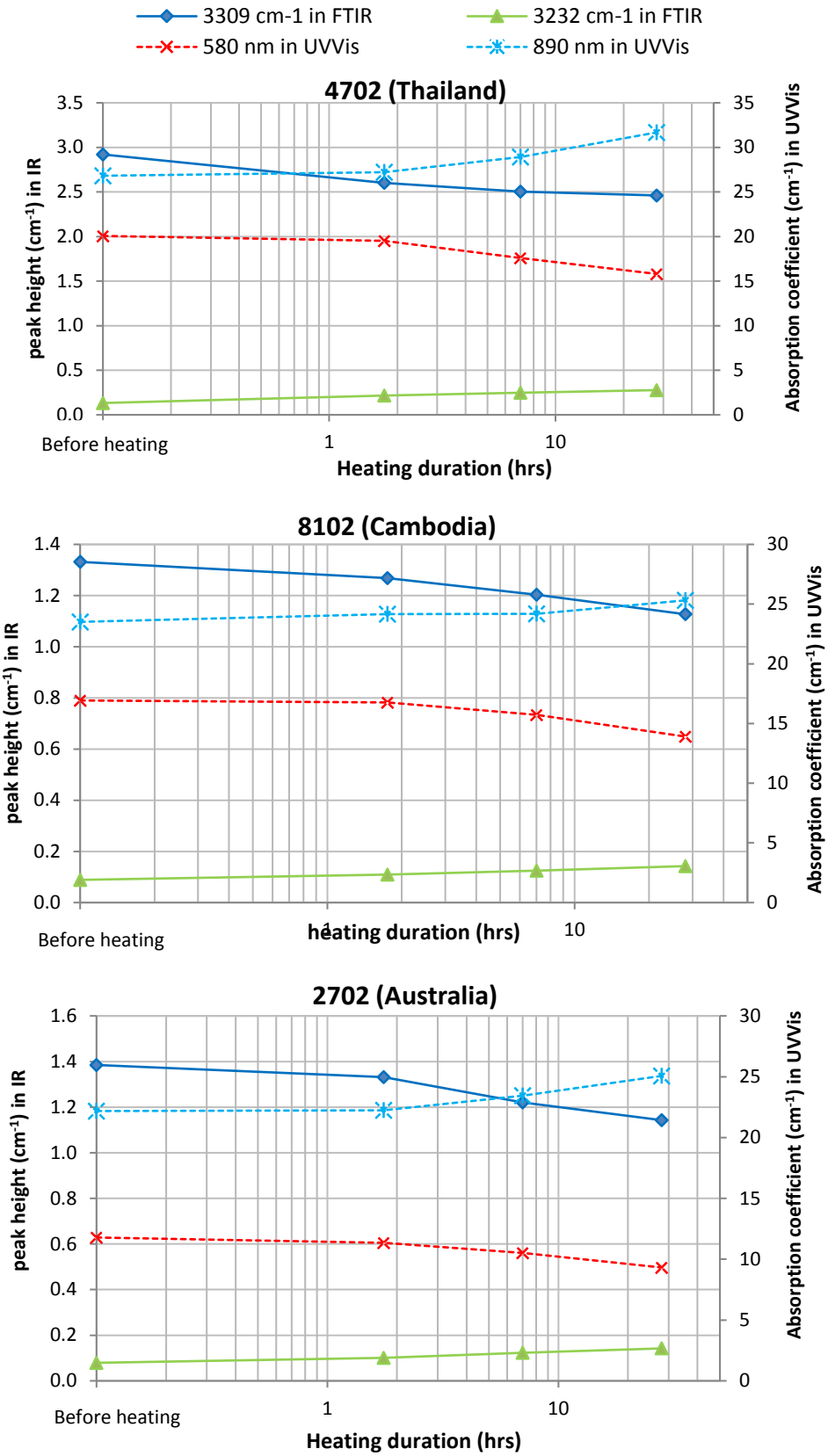


Figure 47: Plots of intensities/heights of UV-Vis-NIR and FTIR features of samples showing lighter blue color after heating at 700 °C at different heating duration in logarithm scale. Intensities of 890 nm in came from the differential spectrum of the samples and pure Fe^{2+}-Ti^{4+} pair of synthetic blue sapphire.

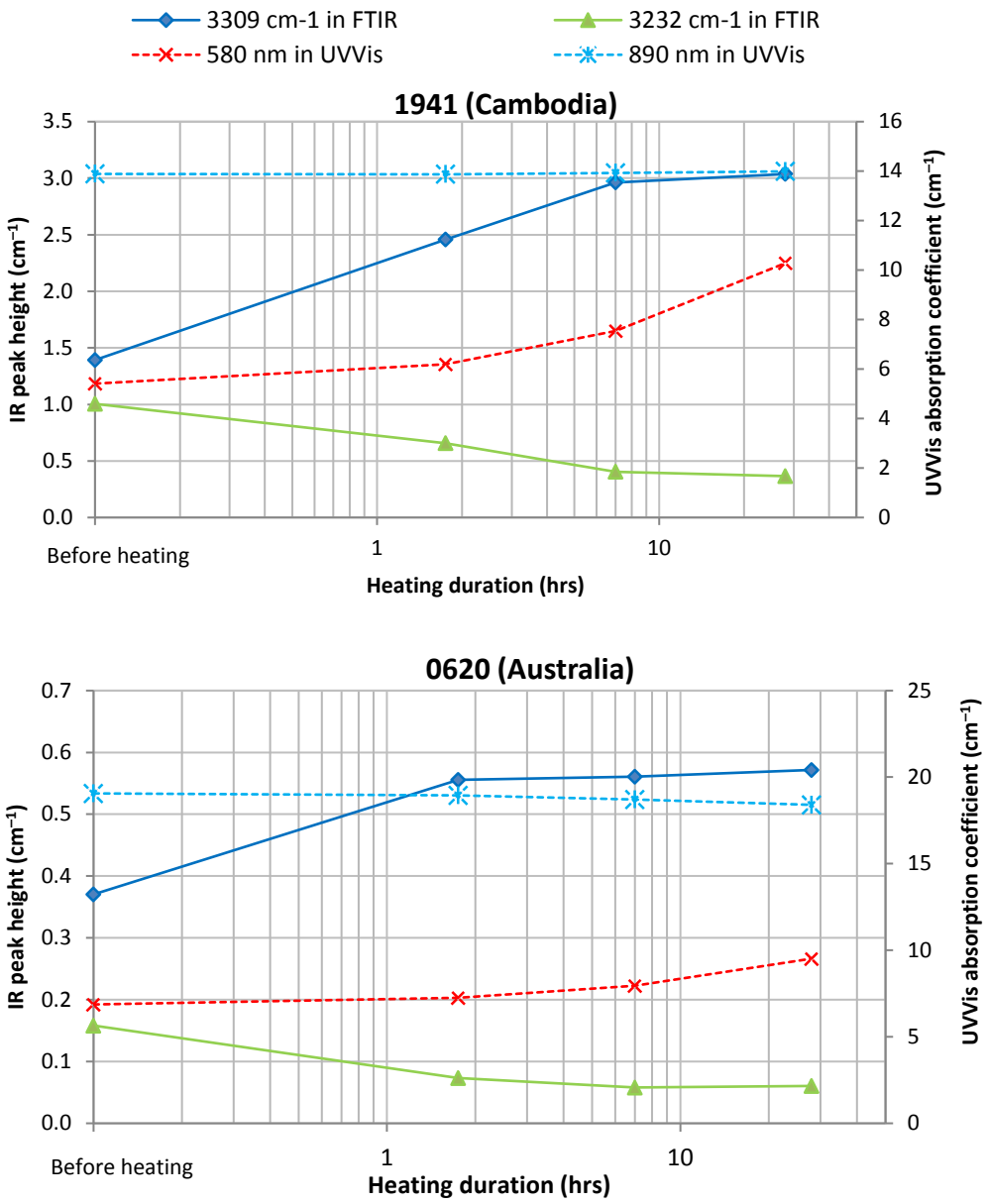


Figure 48: Plots of intensities/heights of UV-Vis-NIR and FTIR features of samples showing stronger blue color after heating at 700°C at different durations in logarithmic scale. Intensities of 890 nm are from the differential spectrum of the samples and pure Fe^{2+}-Ti^{4+} pair of synthetic blue sapphire.

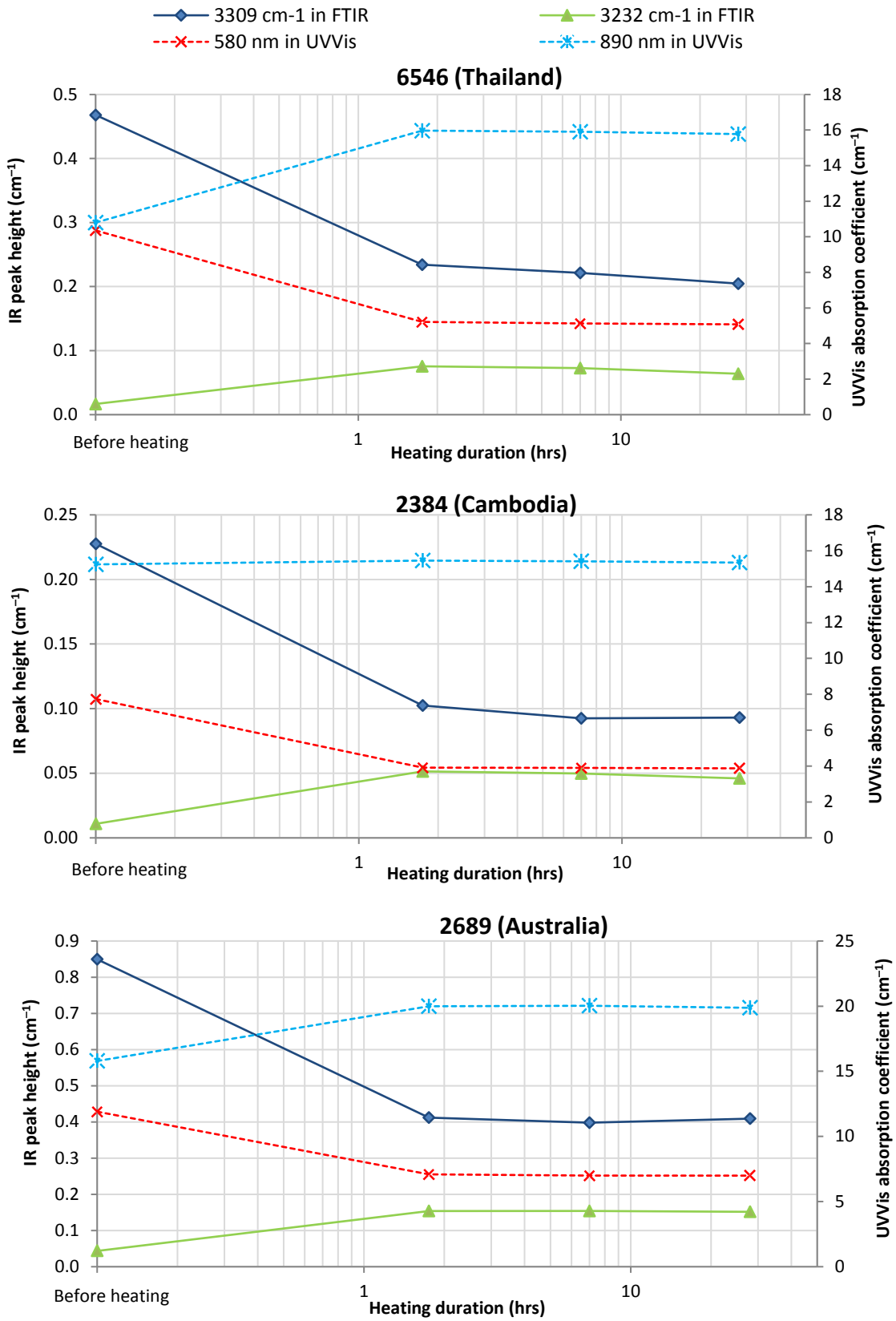


Figure 49: Plots of intensities/heights of UV-Vis-NIR and FTIR features of samples showing lighter blue color after heating at 900°C at different durations in logarithmic scale. Intensities of 890 nm are from the differential spectrum of the samples and pure Fe^{2+}-Ti^{4+} pair of synthetic blue sapphire.

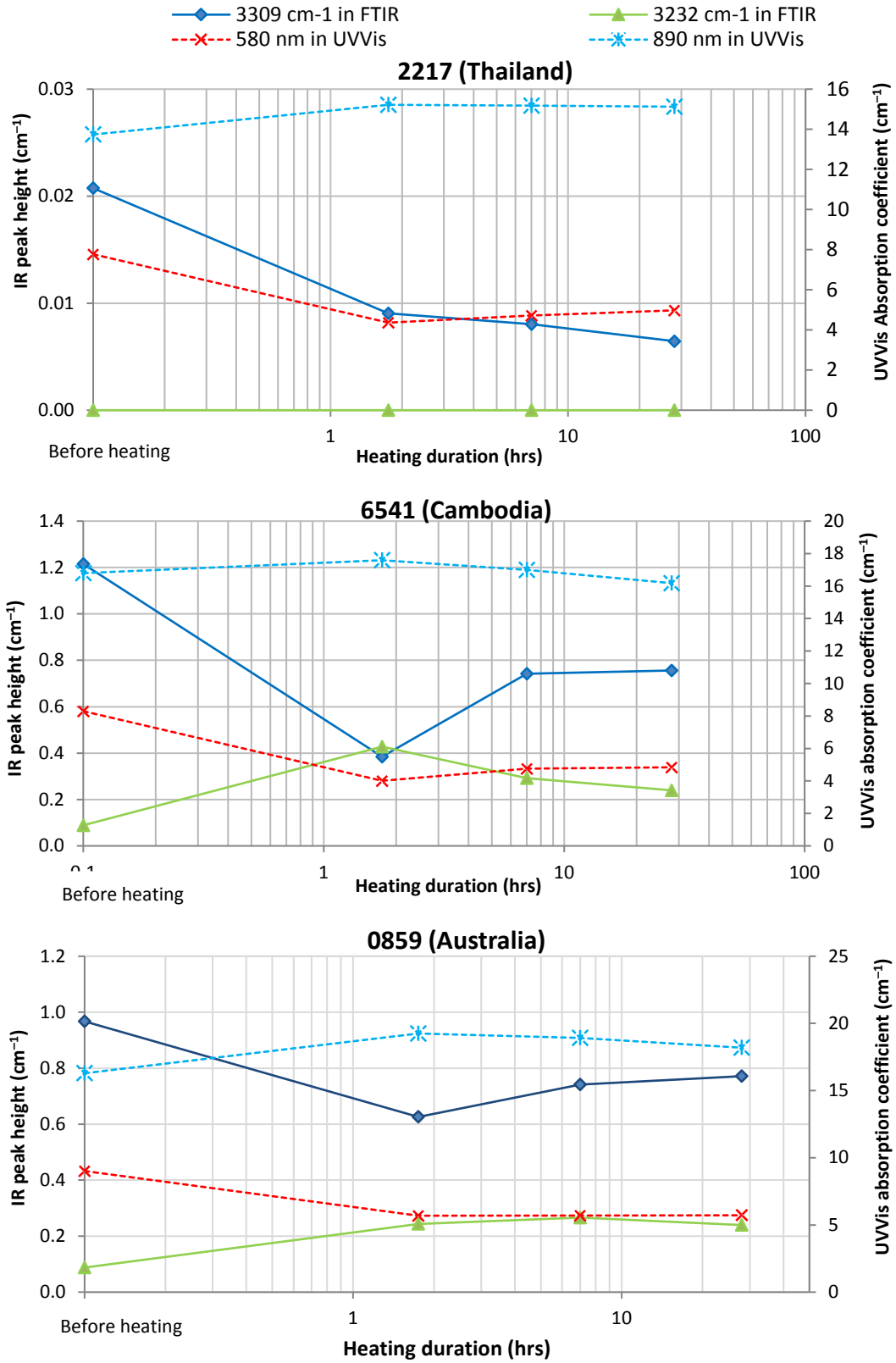


Figure 50: Plots of intensities/heights of UV-Vis-NIR and FTIR features of samples showing lighter blue color after heating at 1050°C at different durations in logarithmic scale. Intensities of 890 nm are from the differential spectrum of the samples and pure Fe^{2+}-Ti^{4+} pair of synthetic blue sapphire.

4. Summary

Low-temperature heat treatment can be used to improve an oversaturated blue color of sapphires from basalt-related deposits, such as Australia, Cambodia, Nigeria, and Thailand. In this study, the reduced blue color of the materials was significantly observed at temperatures of 900°C or above in air or oxidizing conditions. In addition, the blue color was strongly affected by the heating temperature (between 500 and 1500°C) and slightly impacted by the heating duration (1.75, 7, and 28 hours). In some cases, microscopic examination revealed the alteration of inclusions, which may provide sufficient evidence to prove that low-temperature heat treatment has been applied. However, even when comparing the inclusion scenes before and after treatment, separation often remains challenging. The samples showed slightly different fluorescence reactions before and after the heat treatment process. FTIR spectroscopy were also used to investigate the change in spectra before and after heat treatment, and the variable FTIR results were obtained. Therefore, it is still very challenging to distinguish basalt-related blue sapphires that have been heated with low-temperature process from those that have not undergone any post-mining treatment using standard gemological tests and advanced instruments.

Acknowledgments: The authors wish to thank Dr. John Emmett, Mr. Shane McClure, Mr. Nicholas Sturman, for their invaluable advice, guidance, and support. We also thank Mr. Duncan Pay, Mr. Stuart Overlin, Dr. Tao Hsu and Ms. Brooke Goedert for kindly reviewing this report, Ms. Sasithorn Engniwat, Mr. Suwasan Wongchacree, and Ms. Vararut Weeramongkhonlert for their assistance to fabrication and data collection.

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Appendix A: Comparisons of photoinclusions before and after high-temperature heat treatment at 1500°C

In some cases, basalt-related blue sapphires were heat treated at high temperature, approximately around 1400-1800°C, to turn their colors to attractive blue and suitable for the cutting process (Themelis 2010). Seven blue sapphires from basalt-related deposits were heat treated at 1500°C for 7 hours, and the alteration of internal and external features was then recorded. Under short-wave UV radiation, the samples were inert before treatment and three out of seven sapphires exhibited very weak chalky fluorescence after heat treatment.

External feature

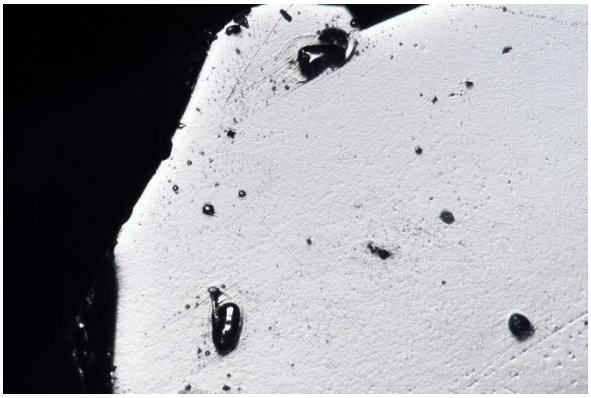

Figure 51: Sample 9300 (Thailand), heated at 1500 °C for 7 hours, *melted/droplet surface*, fiber-optic illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

Internal features

Before heating ***After heating at 1500°C for 7 hours***

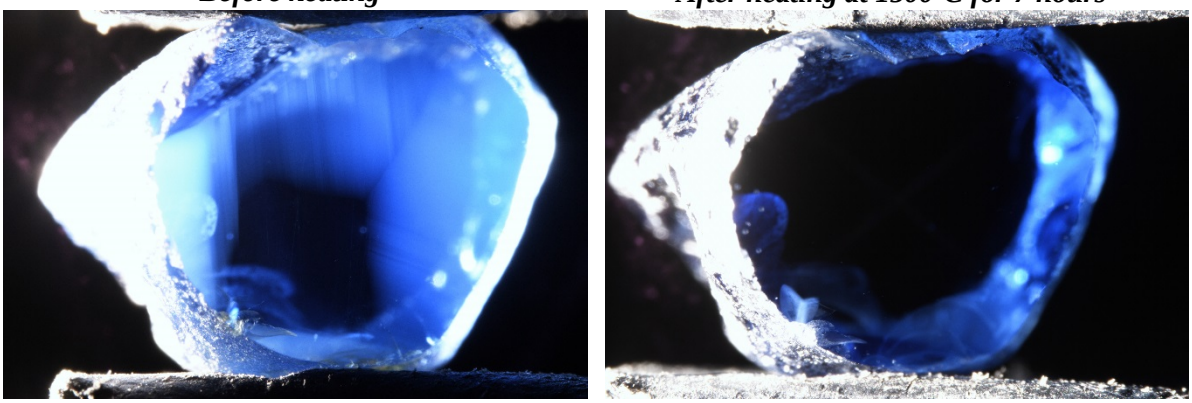

Figure 52: Sample 9492 (Nigeria), heated at 1500°C for 7 hours, *particles dissolved*, fiber-optic illumination, FOV 7.20 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500°C for 7 hours***

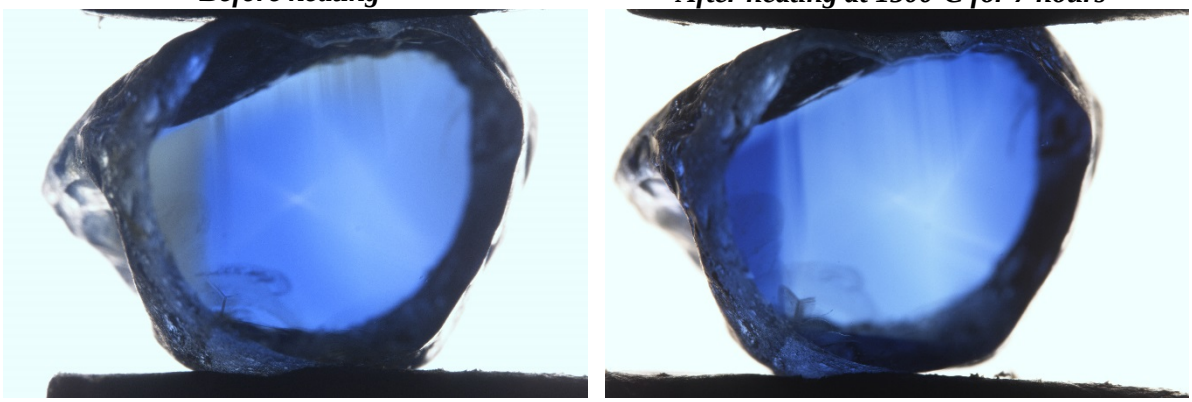

Figure 53: Sample 9492 (Nigeria), same stone as in Figure 52 but different lighting illumination, heated at 1500°C for 7 hours, *internal diffusion on the left-hand side of the stone*, diffused light illumination, FOV 7.20 mm, photomicrographs by C. Khowpong © GIA.

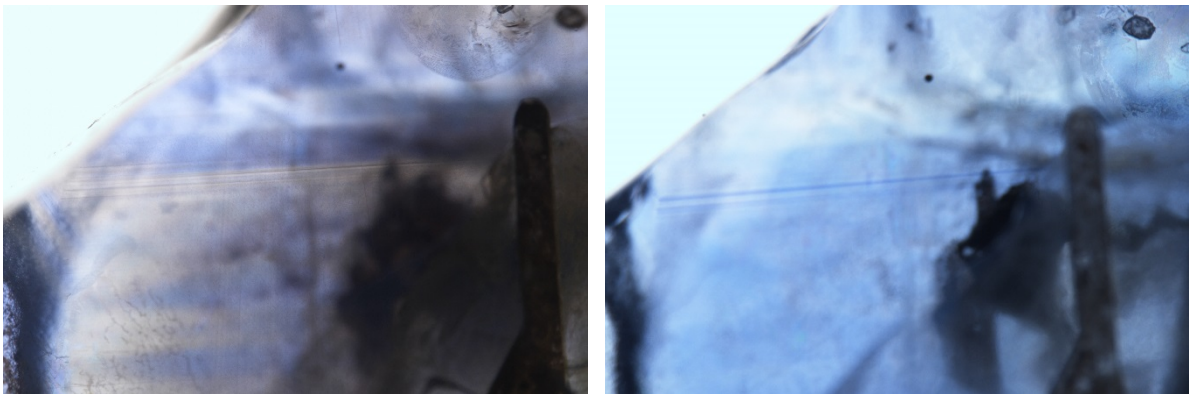

Figure 54: Sample 9129 (Thailand), heated at 1500°C for 7 hours, *internal diffusion*, diffused light illumination, FOV 4.80 mm, photomicrographs by C. Khowpong © GIA.

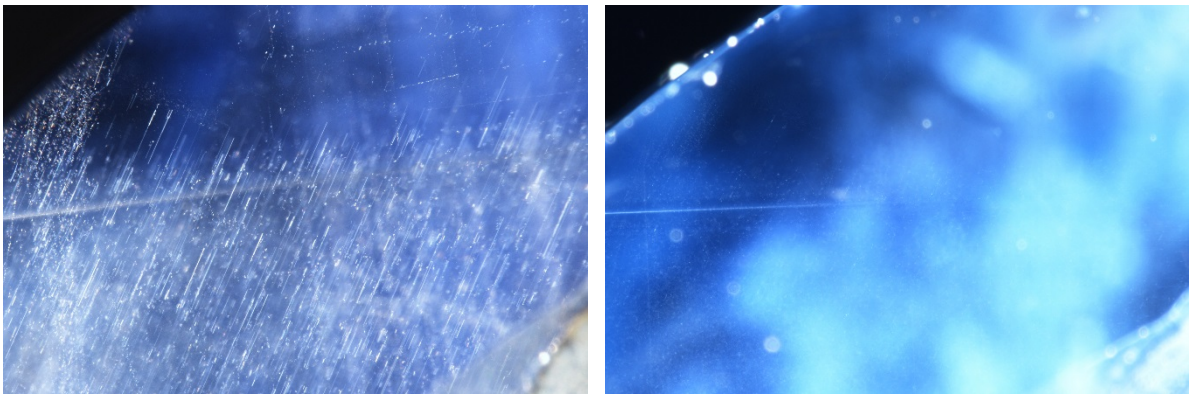

Figure 55: Sample 9129 (Thailand), heated at 1500°C for 7 hours, *needles and particles dissolved*, fiber-optic illumination, FOV 2.85 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500°C for 7 hours***

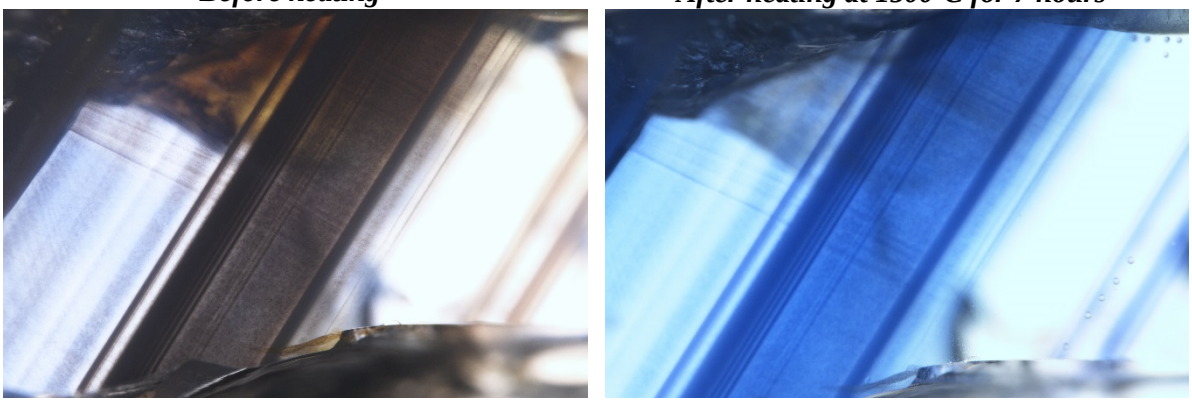

Figure 56: Sample 9300 (Thailand), heated at 1500°C for 7 hours, *internal diffusion*, diffused light illumination, FOV 4.80 mm, photomicrographs by C. Khowpong © GIA.

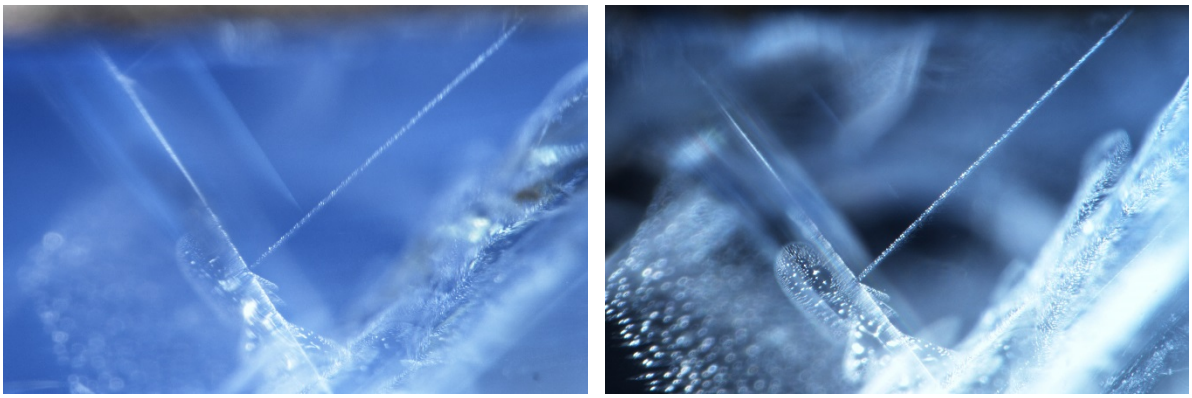

Figure 57: Sample 2390 (Cambodia), heated at 1500°C for 7 hours, *no signs of alteration to tube-like inclusions*, fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

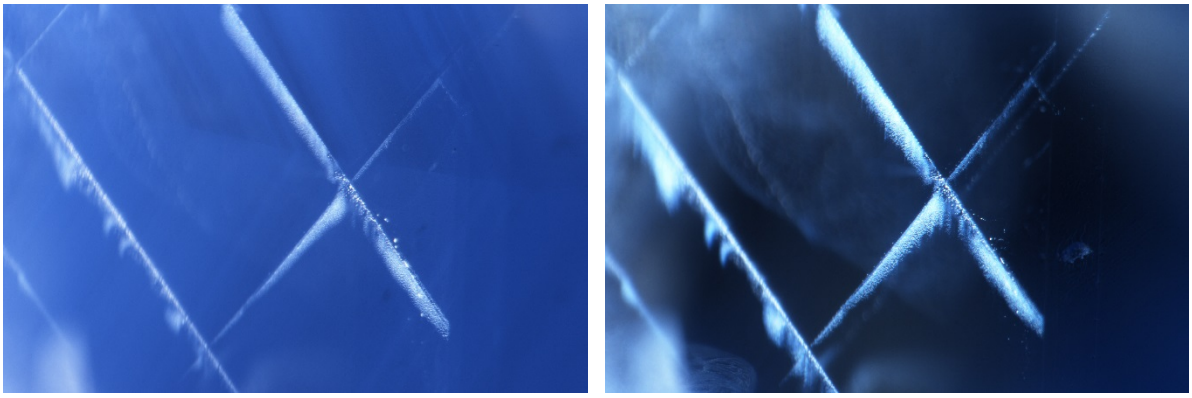

Figure 58: Sample 2390 (Cambodia), heated at 1500°C for 7 hours, *no signs of alteration to growth tubes*, fiber-optic illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500℃ for 7 hours***

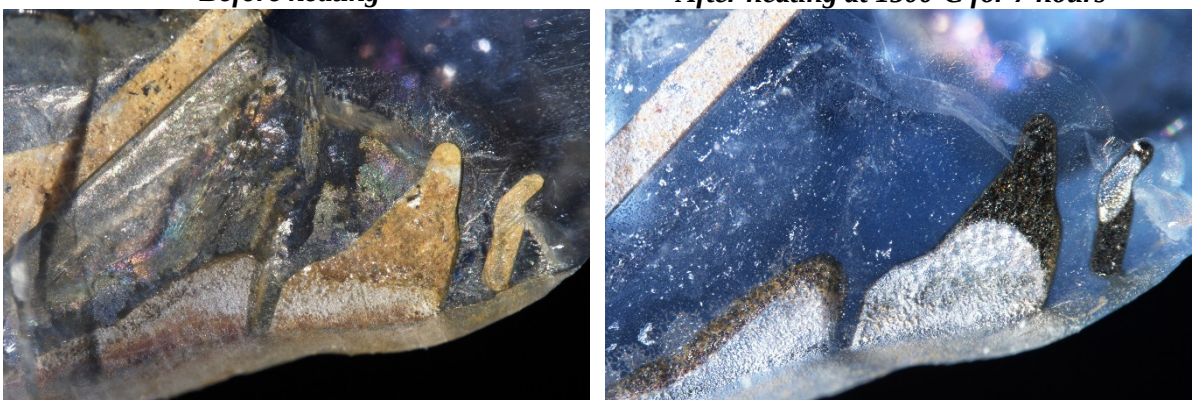

Figure 59: Sample 9129 (Thailand), heated at 1500 °C for 7 hours, *some yellow stain was removed and some changed to black*, fiber-optic illumination, FOV 3.65 mm, photomicrographs by C. Khowpong © GIA.

Figure 60: Sample 9300 (Thailand), heated at 1500°C for 7 hours, *yellow stain along fractures was removed, the black crystal disappeared and fractures changed to dot-like partially healed fractures*, fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

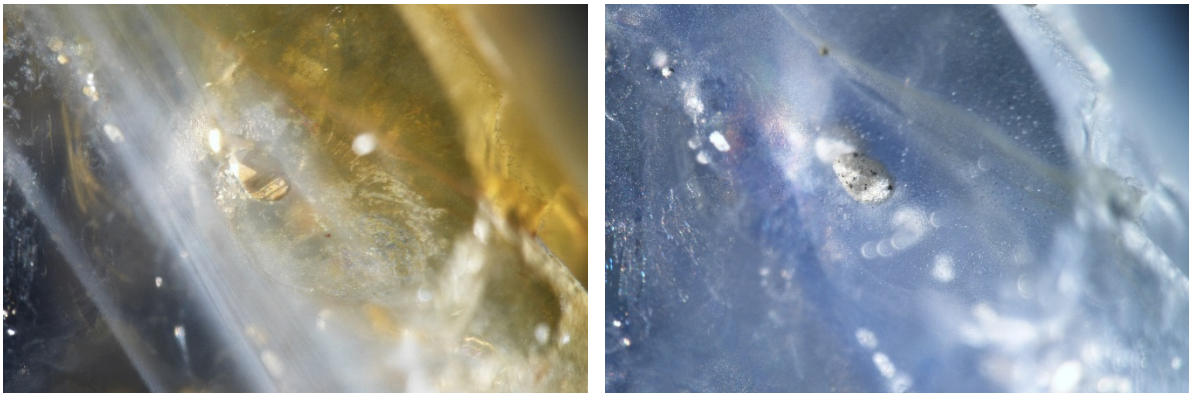

Figure 61: Sample 9300 (Thailand), heated at 1500°C for 7 hours, *the yellow stain was removed and crystal altered to a frosty white form*, fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500°C for 7 hours***

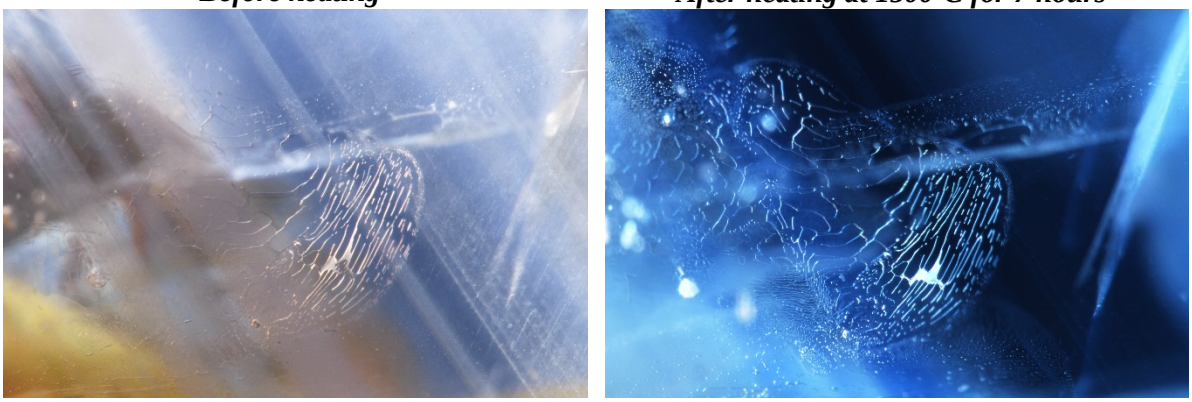

Figure 62: Sample 9300 (Thailand), heated at 1500°C for 7 hours, *minor alteration to a fluid fingerprint and minute particles dissolved,* fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

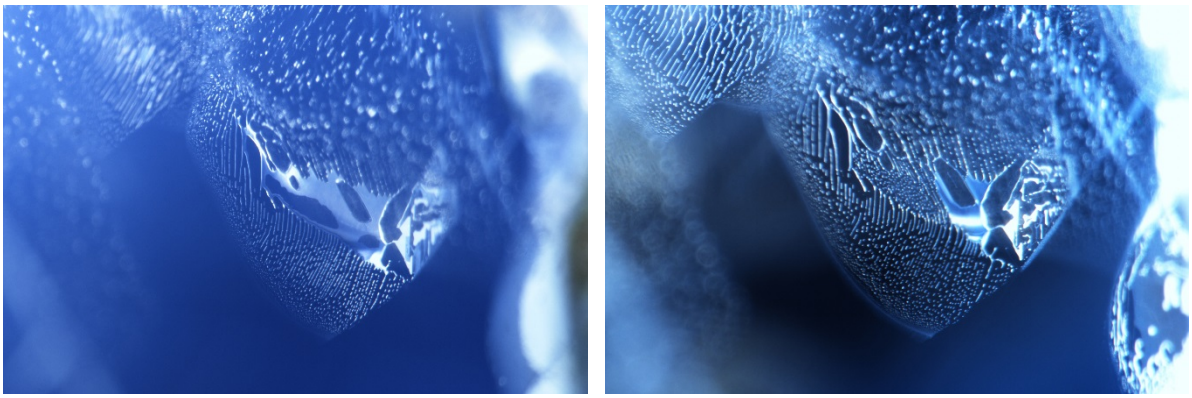

Figure 63: Sample 2390 (Cambodia), heated at 1500°C for 7 hours, *minor alteration to a fingerprint*, fiber-optic illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

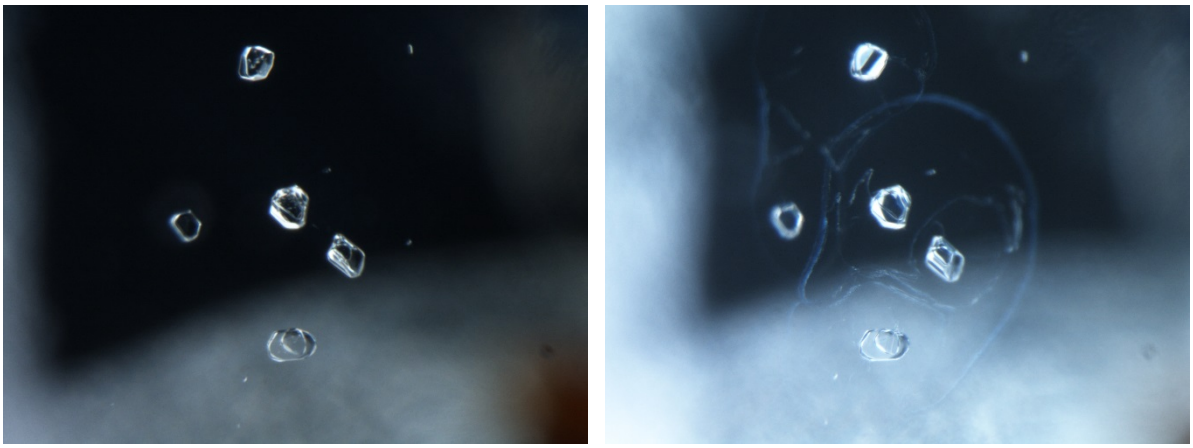

Figure 64: Sample 0626 (Australia), heated at 1500°C for 7 hours, *partially healed fractures developed around feldspar crystals*, darkfield illumination, FOV 1.00 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500℃ for 7 hours***

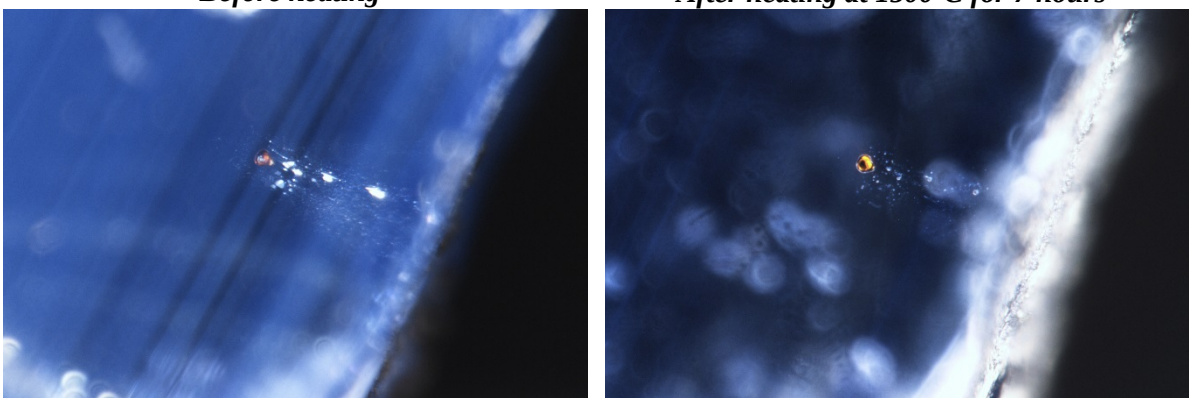

Figure 65: Sample 7159 (Cambodia), heated at 1500°C for 7 hours, *the color of unidentified red crystal, probably pyrochlore, changed to orange*, fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

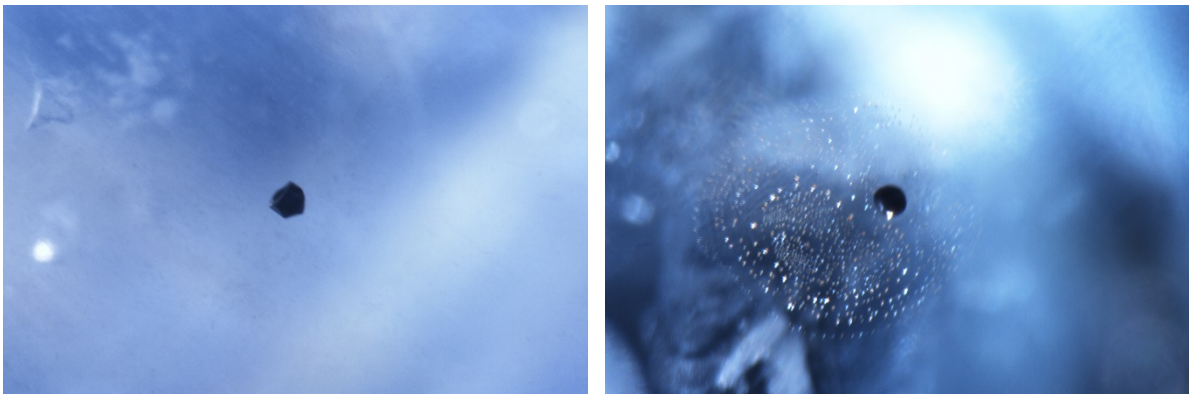

Figure 66: Sample 9129 (Thailand), heated at 1500°C for 7 hours, *the angular ferrocolumbite changed to round shape and dot-like fingerprint developed around the crystal* , darkfield and fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

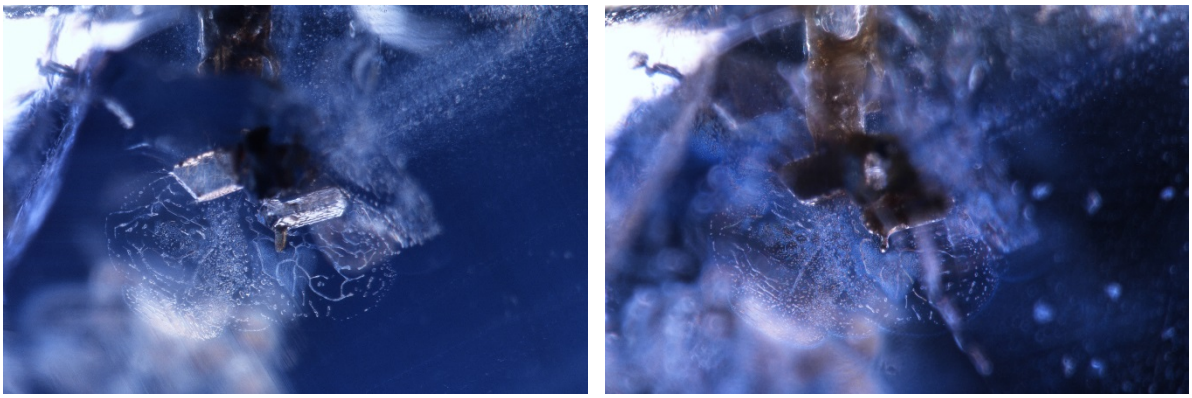

Figure 67: Sample 7159 (Cambodia), heated at 1500°C for 7 hours, *prismatic zircon crystals altered to a frosty form and fingerprints surrounded crystals look altered* , darkfield illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500℃ for 7 hours***

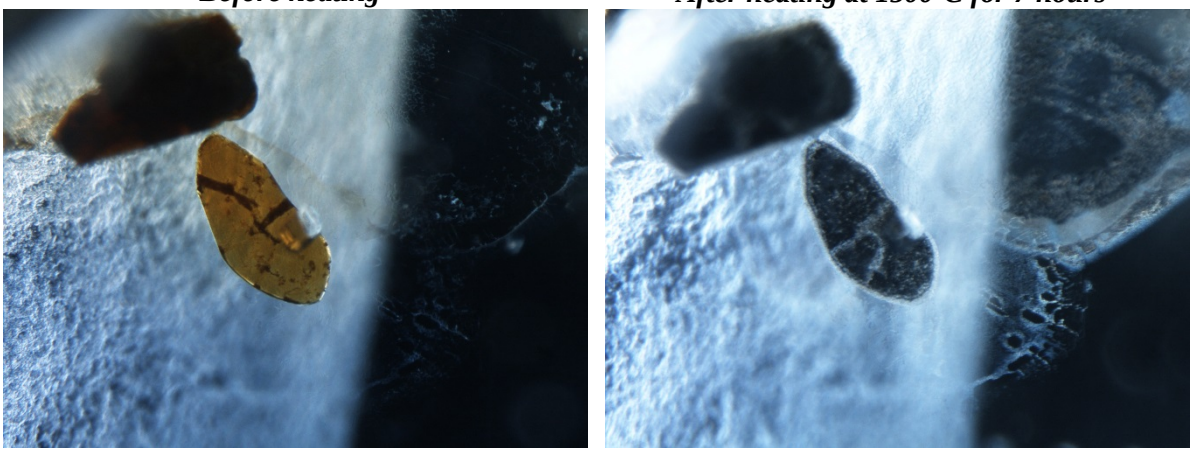

Figure 68: Sample 0626 (Australia), heated at 1500°C for 7 hours, *the unidentified brownish transparent tabular crystal changed to an opaque frosty black form*, darkfield illumination, FOV 1.30 mm, photomicrographs by C. Khowpong © GIA.

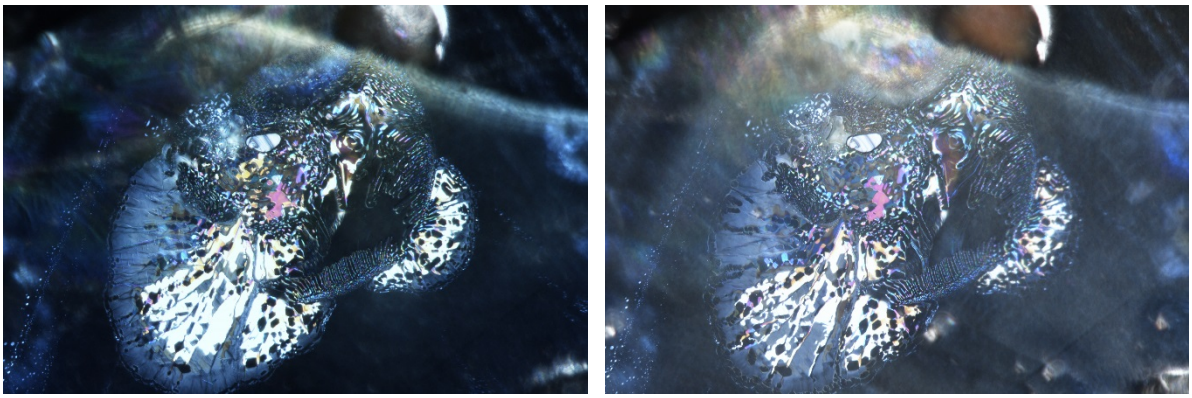

Figure 69: Sample 0626 (Australia), heated at 1500°C for 7 hours, *minor alteration to fluid inclusion*, fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

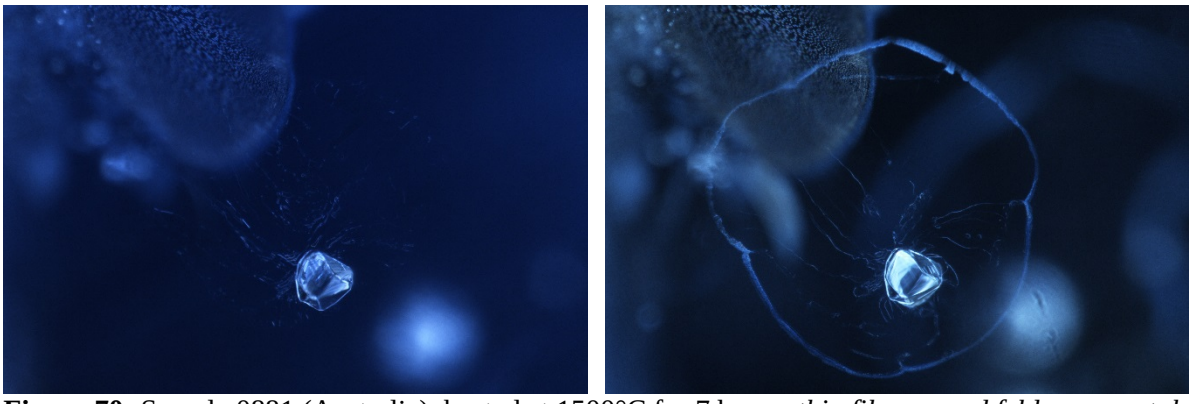

Figure 70: Sample 0881 (Australia), heated at 1500°C for 7 hours, *thin film around feldspar crystal changed to discoid fracture*, darkfield illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500℃ for 7 hours***

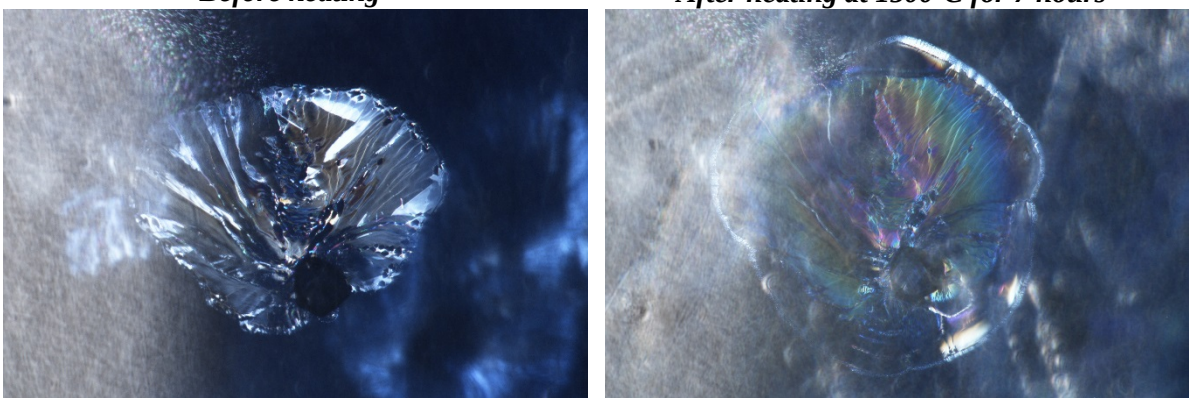

Figure 71: Sample 0881 (Australia), heated at 1500°C for 7 hours, *thin film around feldspar crystal changed to discoid fracture*, fiber-optic illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

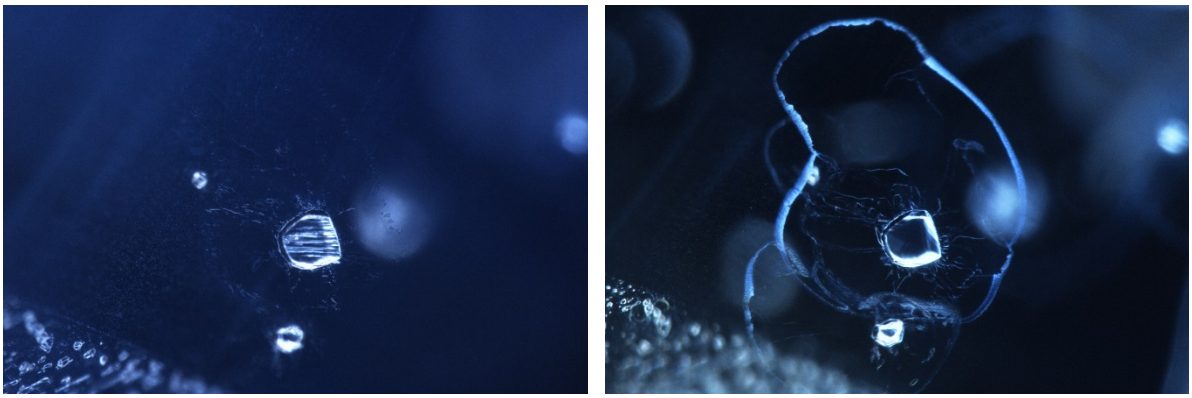

Figure 72: Sample 0881(Australia), heated at 1500°C for 7 hours, *thin film around feldspar crystal changed to discoid fracture*, dark field illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

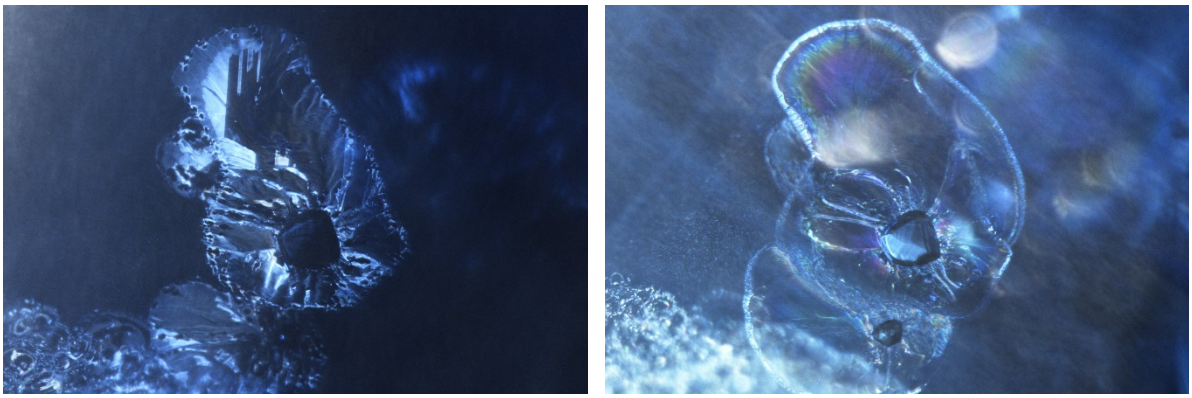

Figure 73: Sample 0881(Australia), heated at 1500°C for 7 hours, *thin film around feldspar crystal altered to discoid fracture*, fiber-optic illumination, FOV 1.75 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500℃ for 7 hours***

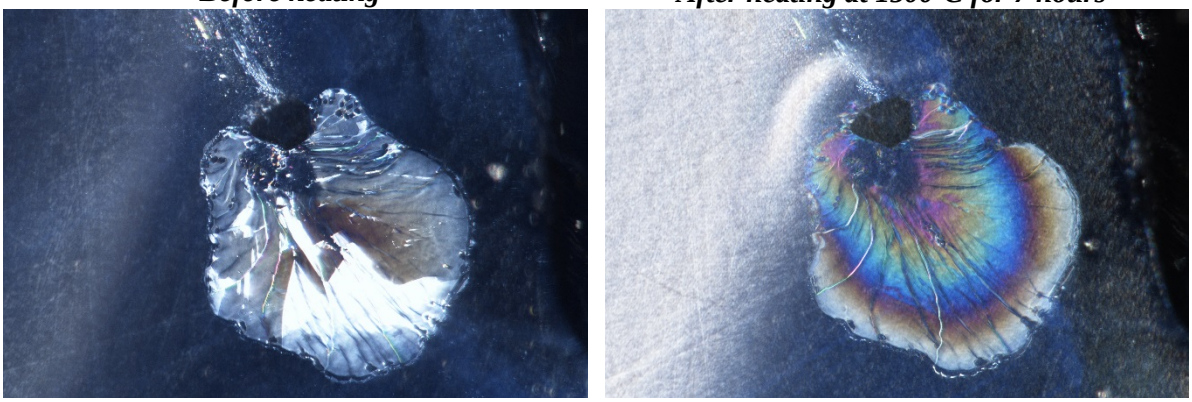

Figure 74: Sample 0881(Australia), heated at 1500°C for 7 hours, *thin film around feldspar crystal altered to discoid fracture*, fiber-optic illumination, FOV 1.40 mm, photomicrographs by C. Khowpong © GIA.

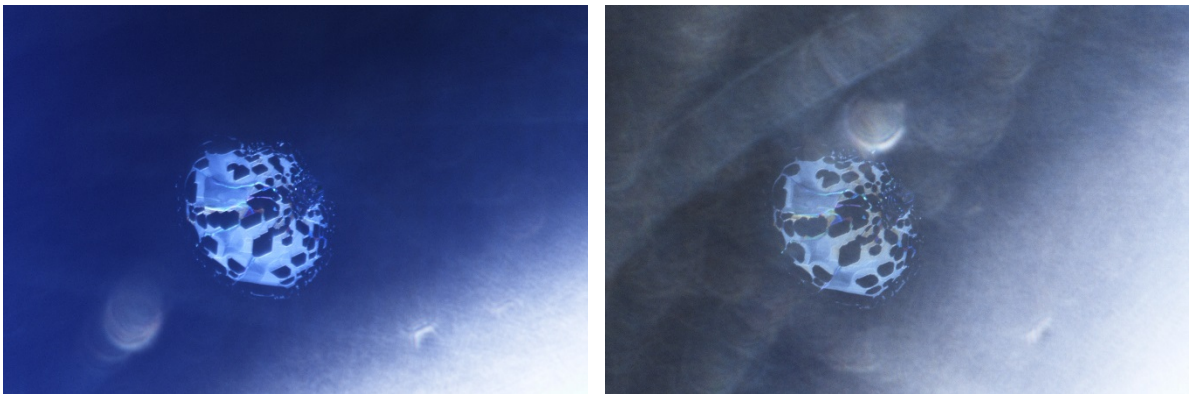

Figure 75: Sample 9492 (Nigeria), heated at 1500°C for 7 hours, *minor alteration to thin film*, fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

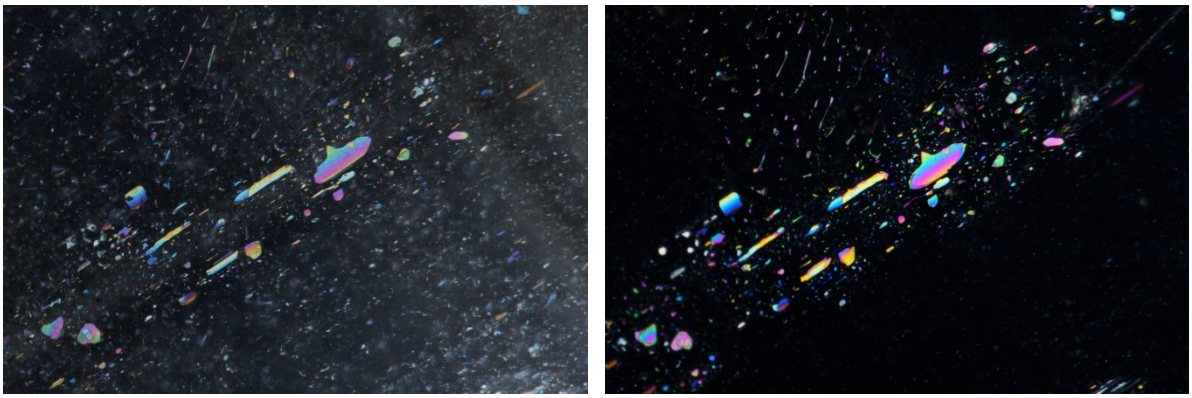

Figure 76: Sample 9300 (Thailand), heated at 1500°C for 7 hours, *no signs of alteration to iridescent thin films*, fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

Before heating ***After heating at 1500°C for 7 hours***

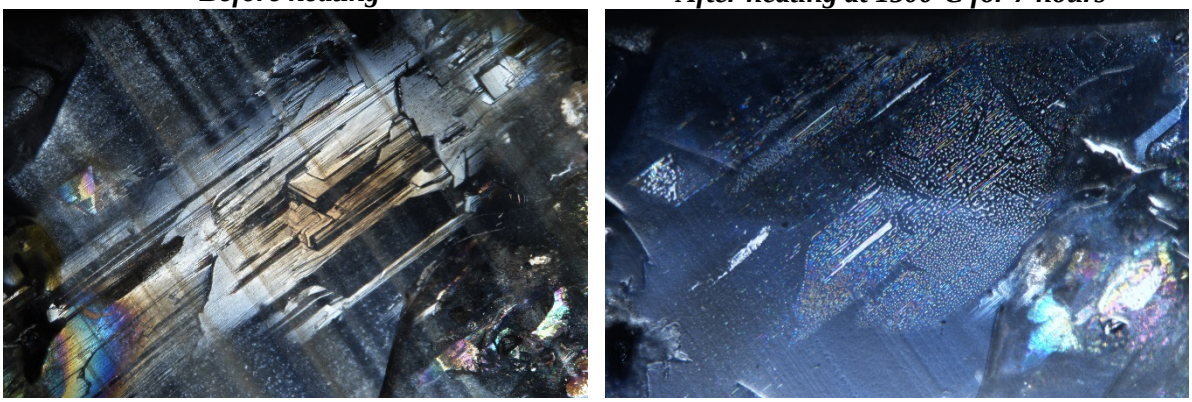

Figure 77: Sample 9300 (Thailand), heated at 1500°C for 7 hours, *iridescent fractures were partially healed,* fiber-optic illumination, FOV 3.65 mm, photomicrographs by C. Khowpong © GIA.

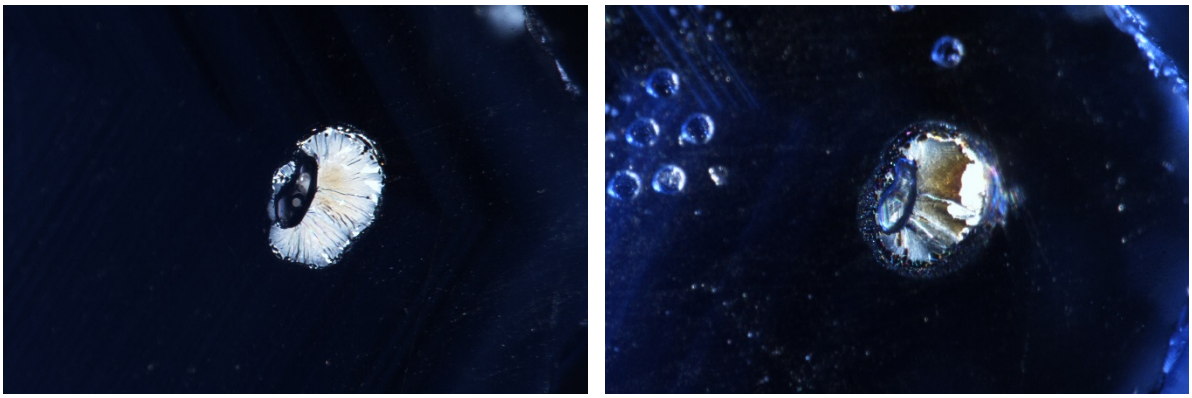

Figure 78: Sample 7159 (Cambodia), heated at 1500°C for 7 hours, *thin film around feldspar crystal developed partially healed fracture at rim*, fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.

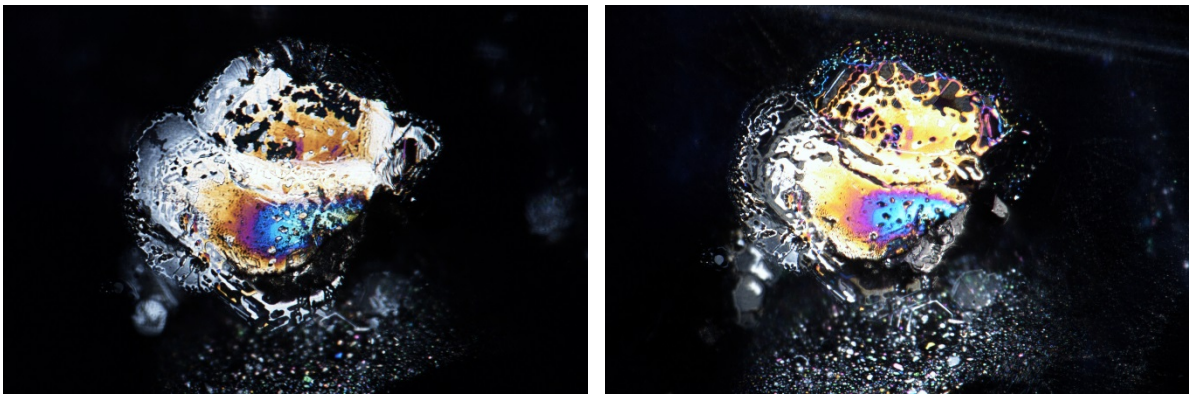

Figure 79: Sample 7159 (Cambodia), heated at 1500°C for 7 hours, *alteration to iridescence thin film at rim*, fiber-optic illumination, FOV 1.05 mm, photomicrographs by C. Khowpong © GIA.