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Discovering Colour Alteration Conditions and Inclusion Changes of Sri Lankan Black/Brown (*Penithora/Maangu*) Tourmaline

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ABSTRACT

Black or brown tourmalines, commonly referred to as "*Penithoora*" or "*Maangu*" in Sinhalese, are predominantly found in Sri Lanka and are primarily used in the production of decorative items due to their limited market demand and lower value as gemstones. This study aims to investigate the conditions under which the color of black/brown tourmaline can be altered through heat treatment, with the objective of maximizing profitability from gem pits. A total of sixty samples of black/brown tourmaline were subjected to heat treatment using a "Lakmini" gas-fired furnace, employing five different temperatures (700 °C, 750 °C, 800 °C, 850 °C, and 900 °C) and varying soaking times of two, three, and four hours under oxidizing conditions within the gas furnace. The samples were subsequently analyzed using Energy Dispersive X-Ray Fluorescence (ED-XRF) spectroscopy and a gemological microscope to assess changes in chemical and optical properties. The results obtained from ED-XRF spectrometry indicated that silicon, aluminium, and magnesium were the major elements, while titanium, iron, and manganese were significant trace elements present in black/brown tourmaline. Minor color reduction was observed at 700 °C, with slight brown color reduction occurring at 750 °C and 800 °C. Significant color reduction coupled with clarity enhancement was achieved at temperatures of 850 °C and 900 °C. By elucidating the color alteration conditions and associated changes in inclusions, this study contributes to the understanding of heat treatment effects on black/brown tourmaline, enabling enhanced identification and potential value optimization of these gemstones. Following the heat treatment, crystal inclusions exhibited a cloudy or partially melted appearance, resembling sugar crystals. Trichites, which exhibited a continuous flow in natural stones, appeared discontinuous after heat treatment. Therefore, heating at 850 °C for a maximum of three hours resulted in a more reduced brown/black translucent appearance with improved clarity.

1. Introduction

The island of Sri Lanka, as documented in the Sri Lankan chronicle "Mahavansa", has historically been renowned for its mineral wealth, earning it the name "Rathna Deepa". The gem and jewelry industry in Sri Lanka has flourished for centuries, with evidence of trade dating back as far as 250 BC. Ceylon, the former name of Sri Lanka, has been a prolific producer of a wide range of gemstones, including sapphires (in blue, golden yellow, pink, orange, Padparadscha, and Star varieties), chrysoberyl cat's eyes, alexandrite, garnets, zircons, tourmalines, and spinels. The chronicle also highlights the practice of Sri Lankan kings sending gems and pearls to foreign countries as a means of establishing trade and diplomatic relationships.

Gem materials utilized in jewelry predominantly originate from inorganic minerals or substances. Meanwhile, gem materials produced by living organisms are categorized separately, and artificially produced substances fall under the classification of artificial products. Tourmaline, a naturally occurring semi-precious gemstone, can be found worldwide and is present in various geological environments. It is commonly encountered as an accessory mineral in granitic pegmatites, as well as in low to high-grade metamorphic rocks and clastic sedimentary rocks (Collins, 2010).

Generally, tourmaline has one of the most complicated chemical formulas of all minerals. A simple generic formula for the tourmaline group is:

$XY_3Z_6\ (T_6O_{18})\ (BO_3)_3V_3W$

where:
$X = Na^{1+}$, Ca^{2+} and K^{1+},
$Y = Fe^{2+}$, Mg^{2+}, Mn^{2+}, Al^{3+}, Li^{1+}, Fe^{3+}, and Cr^{3+},
$Z = Al^{3+}$, Fe^{3+}, Mg^{2+}, and Cr^{3+},
$T = Si^{4+}$, Al^{3+}, and B^{3+},
$B = B^{3+}$,
$V = OH^{1-}$ and O^{2-},
$W = OH^{1-}$, F^{1-}, and O^{2-} (Henry et al., 2011; Collins, 2010).

Most compositional variability occurs at X, Y, Z, W, and V sites; therefore general formula can write as $X_1Y_3Al_6\ (BO_3)_3\ Si_6O_{18}\ (OH, O, F)_4$ (Clarke et al., 1989).

Usually, black/brown tourmalines are not treated; and commonly heat treatment is experienced for pink, olive green, and green varieties (Learned and Faceter, 2011). For example, in Brazil and Mozambique, copper-bearing tourmalines are heat-treated and known as "Paraiba tourmaline." Before treatments, natural copper-bearing tourmalines are violet, blue, purple or red, and after the heat treatment process, it turns into light blue (vibrant turquoise) colour. Heat treatment is done at a fairly low temperature (about 530 ^{0}C) for three hours (Laurs, 2008).

Tourmaline, as a gemstone, exhibits general stability when exposed to light and does not undergo significant changes when exposed to chemicals. However, it should be noted that heat treatments can potentially affect the integrity of tourmaline. High levels of heat can lead to alterations in the gemstone's color, while abrupt temperature changes (thermal shock) can result in fractures within the stones.

Inclusions, which are naturally occurring impurities, are commonly found within gemstones and are formed during the stone's natural formation processes. Some of these impurities contribute to the distinctive value of gemstones. For instance, the presence of an entrapped insect in amber can significantly enhance its worth, while delicate golden needle-like rutile crystals can augment the value of quartz specimens.

Tourmaline preserves their mother–liquor as liquid inclusions, which are very common and diagnostically reliable to the highest degree. Hair–fine tubes, called "Trichites," are common to all tourmalines. They are thread-like capillaries, not oriented, trending irregularly and crossing one another at random, often knotted into networks, and are filled with liquid (Gubelin, 1983).

Black/brown tourmaline (*"Maangu"* or *"Penithora"*) consider a low-quality, untagged gemstone in the tourmaline group, which is more abundant than the other tourmaline verities in Sri Lanka. Nevertheless, rejects by the gem and jewellery industry due to its unpleasant (non-gem quality) appearance. Thus, the study focused on the colour reduction and clarity enhancement of black/brown tourmaline to upsurge the value and, using microscopic image analysis, developed a method to identify heat-treated black/brown tourmalines.

1.1. Cause of the Colour of Tourmalines

The coloration of green verdelite tourmaline and brown dravite tourmaline is attributed to the involvement of iron (Fe) ions in charge transfer processes. Iron oxidation is the primary cause of coloration in tourmaline, with the Fe^{2+} ions being transformed into Fe^{3+} ions through substitution under oxidizing conditions (Bačík et al., 2011).

Manganese (Mn) ions play a crucial role in generating red and pink hues in tourmaline. Mn^{3+} ions exhibit coloration even at significantly lower concentrations compared to Mn^{2+}. The presence of Mn^{3+} ions typically impart a red color to rubellite tourmaline, which is known for its weak magnetic properties.

Among the color-inducing elements, chromium (Cr) is particularly noteworthy, as it is the second most common coloring agent in gemstones after iron. Chromium oxide (CrO) in trace amounts imparts a green color to chrome tourmaline. Additionally, vanadium (V) ions are responsible for the green color observed in certain tourmaline specimens.

Copper (Cu) is occasionally found as a coloring agent in gemstones, primarily contributing to blue hues. Copper ions (Cu^{2+}) present in oxides also impart a blue color to a select few allochromatic gems, including the transparent Paraiba tourmaline (Feral, 2014).

2. Methodology

The study utilized samples obtained from Ratnapura, Sri Lanka (Fig. 1), which is renowned as a significant locality for gemstones. Upon initial examination, the samples exhibited a black coloration with a dull and opaque appearance. However, when observed under transmitted light, an orangish-brown color became visible along the optical axis. The hardness of the samples, as assessed by the Mohs hardness scale, was determined to be seven.

To facilitate the research, the collected samples were divided into five groups using a random sampling method. Each group consisted of nine specimens, which were subjected to distinct heat treatment conditions. To accurately identify any color changes, the specimens were cut into two pieces, with one piece designated for heat treatment and the other maintained in its pristine state. Additionally, the specimens were polished to create two parallel faces, ensuring optimal visualization of color alterations. The resulting thin sections had an approximate thickness of two millimeters.

Before and after the heat treatment, the samples were examined using a gemological microscope (A. KRUSS Optronic GmbH) under a magnification of 40X. This allowed for precise observation of any color variations. The GIA (Gemmological Institute of America) color grading system was employed to quantify and assess the observed color changes.

The heat treatments were conducted utilizing a "Lakmini" gas furnace, which is a commonly employed furnace by gem traders in Sri Lanka. The furnace allowed for controlled atmospheric conditions and offered a maximum temperature of 1900 °C.

The heat treatments involved three different soaking times (2, 3, and 4 hours) and five maximum temperatures (700 °C, 750 °C, 800 °C, 850 °C, and 900 °C). Oxidizing conditions were maintained within the furnace during the treatments. To examine the effects of heat treatment, the samples were analyzed both before and after the treatment using Gemmo-FTIR™ (Fourier transform infrared spectroscopy). This analytical technique enabled the identification of any spectral changes occurring in the samples as a result of the heat treatment.

Fig. 1. Sampling locations of black/brown tourmaline

Additionally, the samples underwent analysis using ED-XRF (Energy Dispersive X-ray Fluorescence) spectroscopy with the Rigaku NEX CG™ instrument. This analysis allowed for the determination of the chemical composition and nature of the gemstones. By employing these analytical methods, the study aimed to gain insights into the alterations induced by heat treatment on the samples, both spectroscopically through Gemmo-FTIR™ and chemically through ED-XRF spectroscopy.

3. Results and Discussion

3.1. Heat Treatment

Two preliminary heat treatments were conducted in order to determine the optimal atmospheric conditions for inducing color alterations within the furnace chamber. The results indicated that oxidizing conditions were the most suitable for achieving the desired effects. At a temperature of 700 °C, a minor reduction in color intensity was observed. At both 750 °C and 800 °C, a slight brown color reduction was noted. However, significant brown color reduction accompanied by enhanced clarity was observed at temperatures of 850 °C and 900 °C. The color changes were evaluated using the GIA (Gemological Institute of America) color grading system. At 850 °C, the observed color was determined to be Y 8/8. Beyond 900 °C, it was observed that all samples tended to melt, indicating the limitation of higher temperatures for the stability of the tourmaline specimens.

Fig. 2 provides a summary of the color changes observed in the tourmaline specimens under oxidizing atmospheric conditions within the furnace. The results indicate the potential for achieving desired color alterations with a soaking time of 3 hours at temperatures ranging from 750 °C to 900 °C.

3.2. XRF Analysis

The XRF (X-ray Fluorescence) technique is widely employed in the gem industry for the purpose of identifying the chemical composition of gemstones and detecting diffusion-like treatments. In this study, all the samples were analyzed using an ED-XRF elemental analyzer (Rigaku NEX CG ™) to determine their elemental composition.

The major oxides detected in the samples were SiO_2 (silicon dioxide), Al_2O_3 (aluminum oxide), and MgO (magnesium oxide). Additionally, minor oxides such as TiO_2 (titanium dioxide), V_2O_5 (vanadium pentoxide), Cr_2O_3 (chromium oxide), MnO (manganese oxide), Fe_2O_3 (iron oxide), Co_3O_4 (cobalt oxide), NiO (nickel oxide), CuO (copper oxide), and ZnO (zinc oxide) were also identified. Fig. 2 presents a visual representation of the chemical composition changes observed in the natural black/brown tourmaline samples. This analysis provides valuable insights into the elemental makeup of the tourmaline specimens studied.

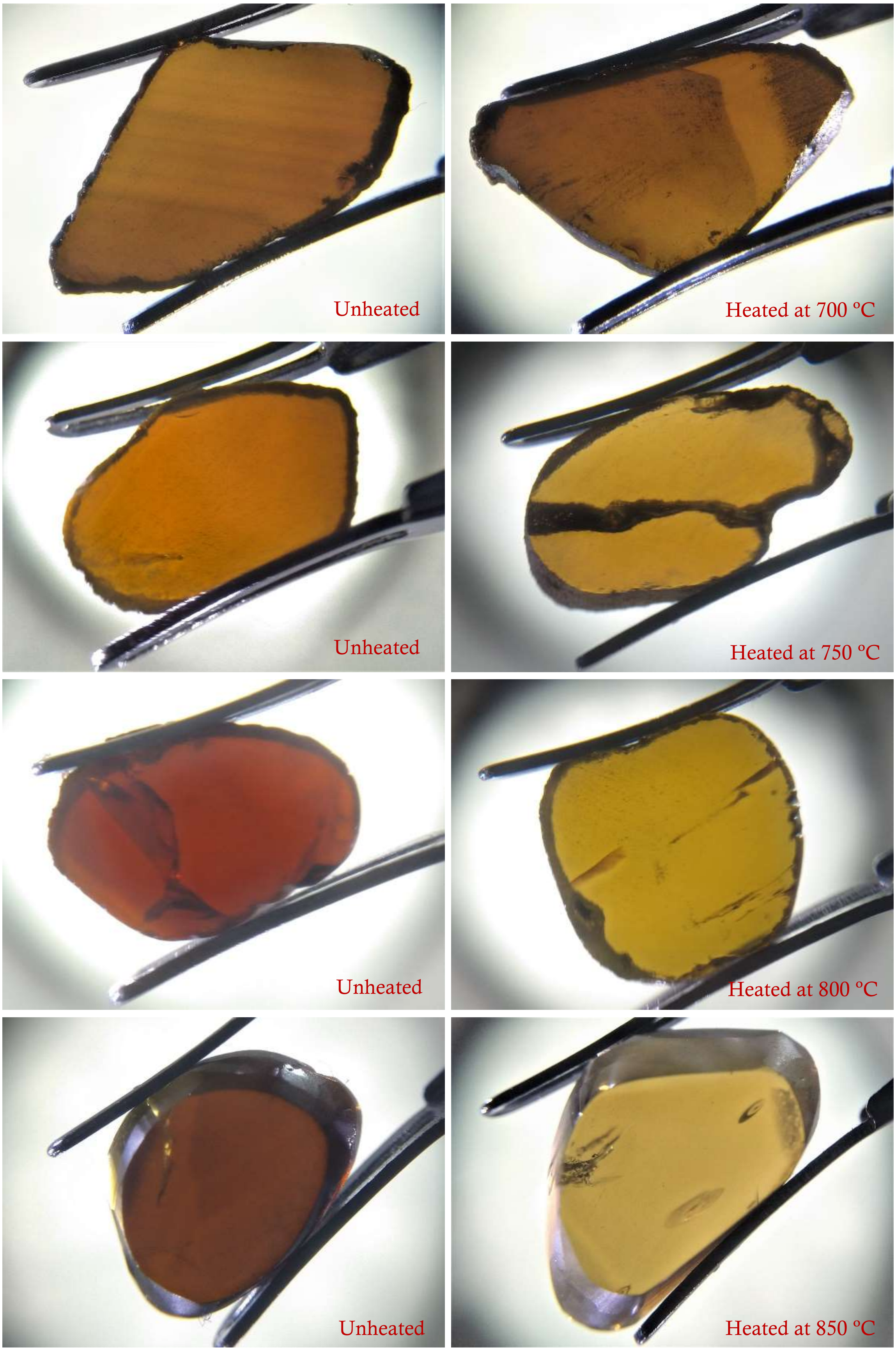


Fig. 2. Colour alteration under different temperatures for 3 hours of soaking time

3.3. FTIR Analysis

Gemmo-FTIR™ equipped with a gold-coated DRIFT (Diffuse Reflectance for Infrared Fourier Transform Spectroscopy) mirror system was used for the FTIR analysis with the wavelength resolution of 15 cm^{-1}. Fig. 4 shows the FTIR spectroscopy observations for the '*Maangu*' tormaline samples.

Absorption peaks at 3800 cm^{-1} to 3300 cm^{-1} corresponded to the vibration mode of OH^- (Filip et al., 2012; Yingmo et al., 2018). The inner hydroxyl group can easily distinguish from low-intensity bands at high wavenumbers (>3600 cm^{-1}) and from three outer ones which produce broad high-intensity low wavenumber bands (3600 $cm^{-1} < \upsilon OH < 3300 cm^{-1}$; υ OH = stretching vibrational bond) (Gonzalez-Carreno et al., 1988) (Fig. 4). After the heat treatment peak at 3410 cm^{-1} has got developed, which is correspond to the vibrational stretching mode of OH^-. All heat treatments were carried out in a gas furnace; therefore, atmospheric hydrogen can be diffused into the crystal and appear to develop the OH^- related peak in the absorption spectrum.

The peaks between 1272 cm^{-1} to 1387 cm^{-1} are linked to the υ_{as} BO_3 (υ_{as} = Asymmetric stretching vibrations), which was noted in unheated samples; however, relevant peaks could not be observed in the heated samples. This may be due to the destruction of BO_3 bonds due to high-temperature heat treatment. Moreover, at the highest temperature treatments, a peak could observe at the wavelength of 1038 cm^{-1}, which characterises the υ_{as} O-Si-O, and the peaks at 601 cm^{-1} to 592 cm^{-1} (~597) signifies the δ Si-O (δ = Deformation vibrations) (Shen et al., 2010).

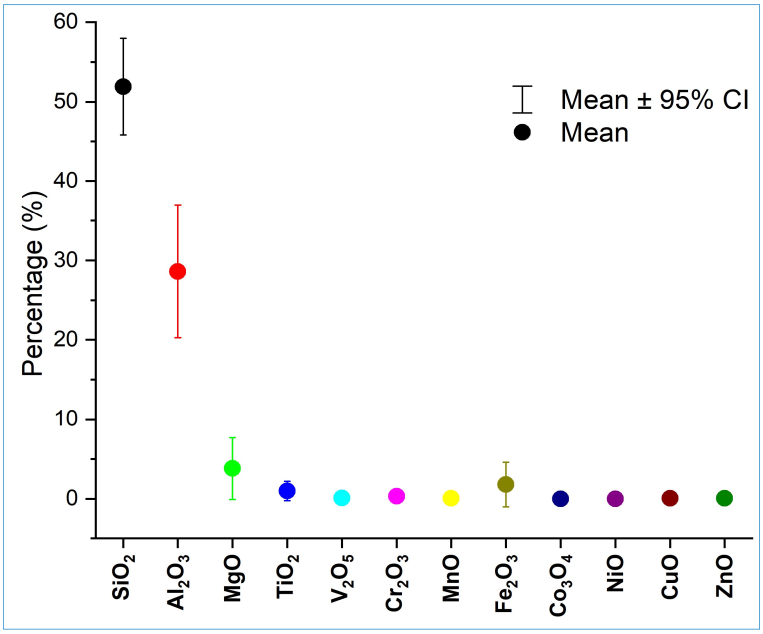


Fig. 3. XRF analysis of black and brown tourmaline

The peak around 1380 cm^{-1} indicates the presence of Mg^{2+} at two Y sites adjacent to O(2), also bonded to B^{3+} whereas a band at around 1340 cm^{-1} is typical for the presence of Mg^{2+} and Al^{3+}at two Y sites.

Further, many vibration modes were observed in the range of 800–350 cm^{-1}. δ BO_3 observed between 800-600 cm^{-1}, Symmetric Si-O-Si band exists at around 700 cm^{-1}. $\nu_{\text{Mg-O}}$, $\nu_{\text{Al-O}}$ and $\delta_{\text{Si-O}}$, and several δ_{OH} were presented below 600 cm^{-1} (Robert et al., 1996). The summary of the FTIR peaks observed in the '*Maangu'* tourmaline is tabulated in Table 1.

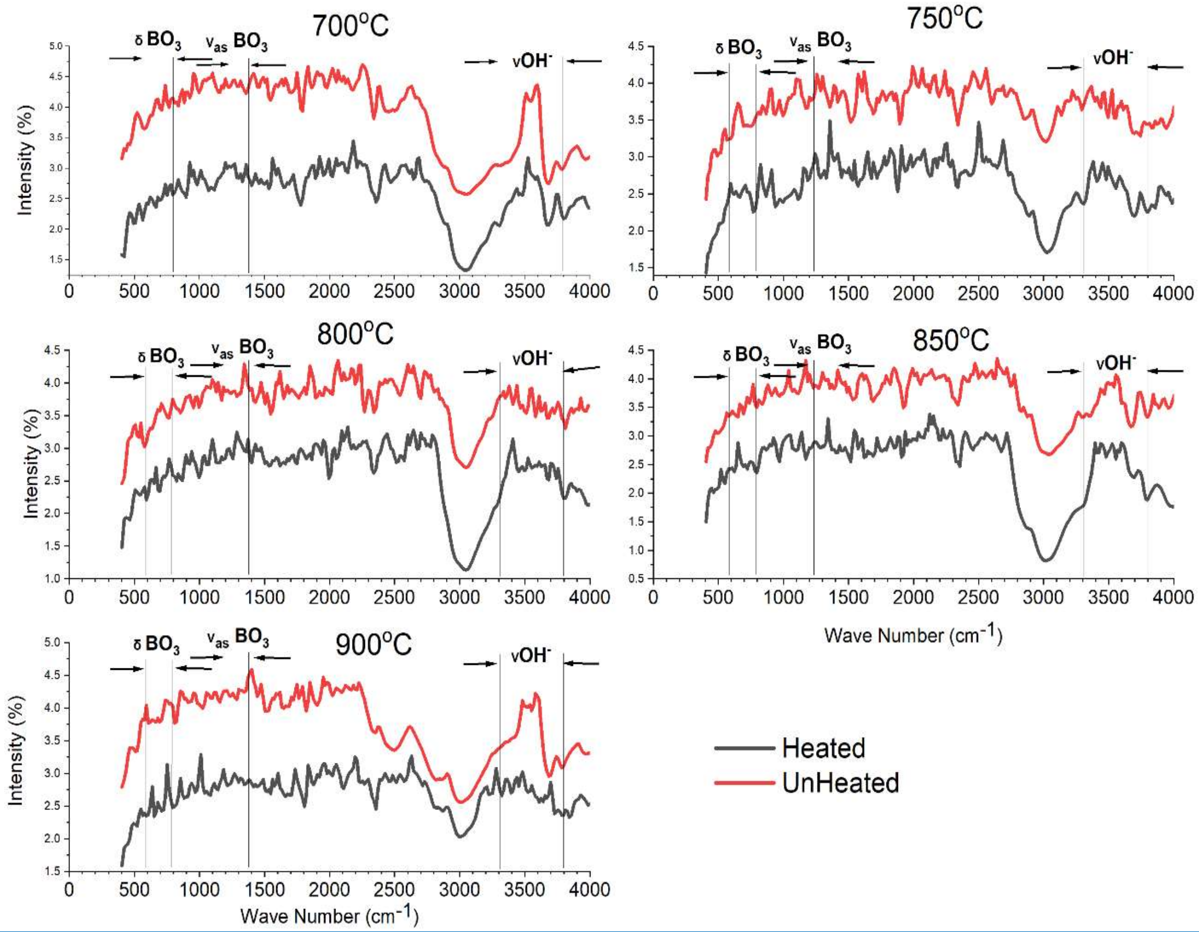


Fig. 4. FTIR spectra of '*Maangu*' tourmalines

Table 1. FTIR Vibrational Modes of *"Maangu"* Tourmaline

Wave number/range (cm^{-1})	Vibrational mode	Reference
592-601	δ Si-O	Shen et al., 2010
600-800	δ BO_3	Robert et al., 1996
700	υ Si-O-Si	Robert et al., 1996
1038	ν_{as} O-Si-O	Shen et al., 2010
1340	Mg^{2+} / Al^{3+}	Robert et al., 1996
1380	B^{3+}	Robert et al., 1996
1272-1387	υ_{as} BO_3	Shen et al., 2010
3300-3800	υ OH	Gonzalez-Carreno et al., 1988; Filip et al., 2012

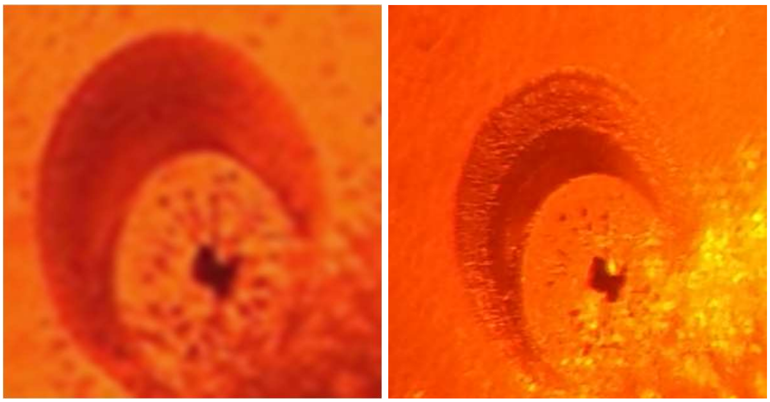
3.4. Inclusions Changes in Tourmaline

Out of the total of sixty thin sections examined, twenty-four sections were found to contain inclusions, fifteen sections exhibited clarity without any cracks or inclusions, and twenty-one sections showed the presence of cracks. Among the sections with inclusions, ten contained crystals, eight had trichites (thread-like or fine hair-like inclusions often filled with liquid and/or gas), and one section contained a bi-phase inclusion.

The identified inclusions included trichites, two-phase inclusions, and some solid crystals. The unheated portion of one tourmaline slice exhibited irregularly shaped cavities filled with liquid, a characteristic previously reported by Laurs et al. (2008) in various tourmaline varieties. Moreover, the majority of the inclusions observed were isolated and transparent in nature.

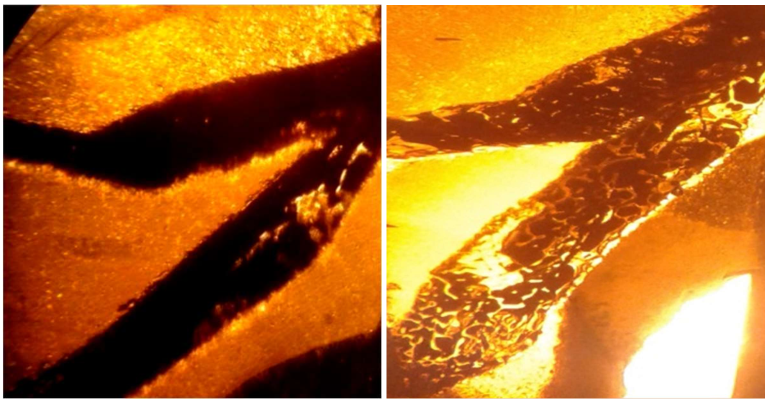
Fig. 5 provides an overview of the behavior exhibited by the inclusions before and after the heat treatment process. It was noted that the flow of trichites became discontinuous, and the crystals exhibited a cloudy appearance with partial melting, including the presence of cracks. The heat treatment process led to significant changes in most of the inclusions, offering potential indications for distinguishing heated stones from unheated (natural) gemstones.

Type of Inclusion: Trichites



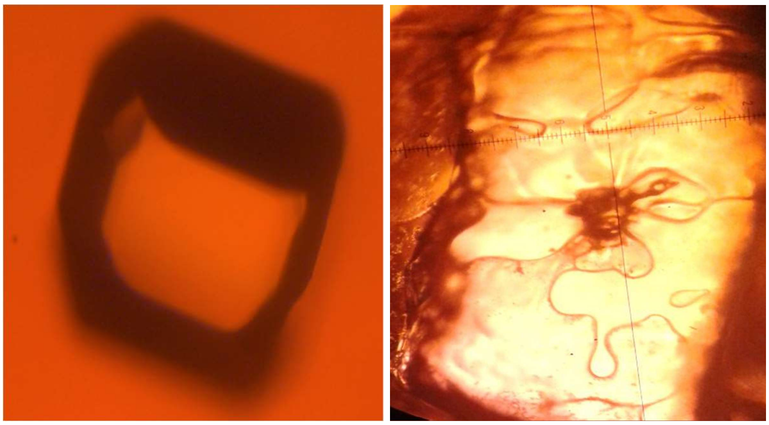
Unheated *Heated at 800 °C*

Type of Inclusion: Crack



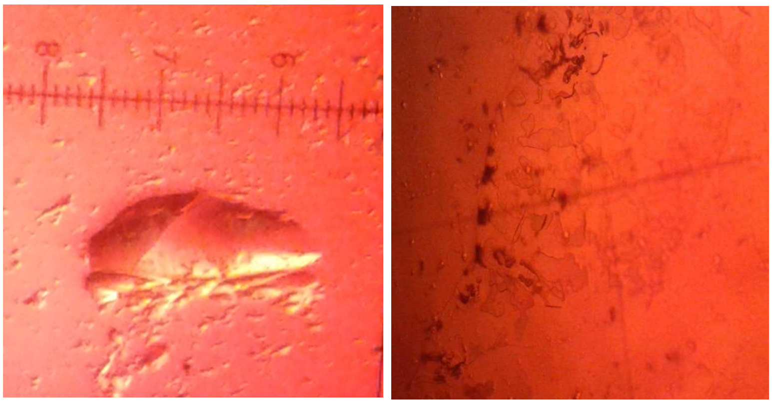
Unheated *Heated at 850 °C*

Type of Inclusion: Tabular shape solid crystal



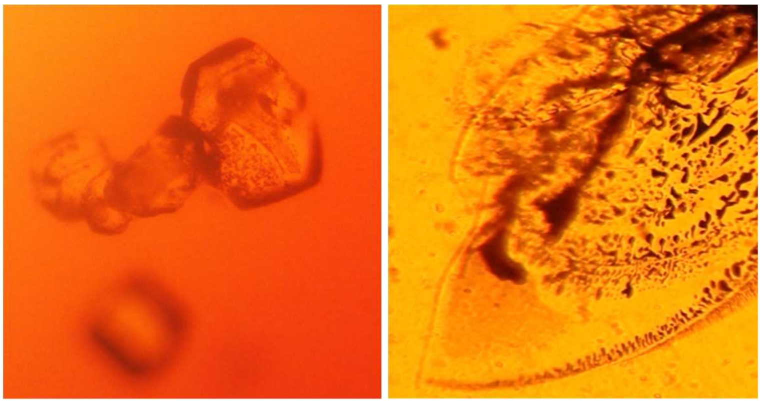
Unheated *Heated at 750 °C*

Type of Inclusion: Solid crystal



Unheated *Heated at 800 °C*

Type of Inclusion: Clustered solid crystal



Unheated *Heated at 750 °C*

Type of Inclusion: Rainbow-coloured bi-phase liquid-gas inclusion

Fully melted after the heat treatment process without a trace

Unheated *Heated at 900 °C*

Fig. 5. Behaviour of the inclusions before and after heat treatment

4. Conclusion

The samples underwent heat treatment at various temperatures: 700°C, 750°C, 800°C, 850°C, and 900°C, for durations of 2, 3, and 4 hours. The results showed a minor reduction in color intensity at 700°C, while a gradual brown color reduction was observed at 750°C and 800°C. Significant color reduction accompanied by enhanced clarity was achieved at 850°C and 900°C. Therefore, the optimal temperature and soaking time to enhance the hue, saturation, and tone of "Maangu" or brown tourmaline was determined to be 850°C with a three-hour soaking time. Based on the XRF analysis, Silicon (Si), Magnesium (Mg), and Aluminium (Al) were identified as the major elements in the "Maangu" tourmaline. Additionally, trace elements such as Titanium (Ti) and Iron (Fe) were also present. Notably, Iron (Fe) was identified as the element responsible for the coloration of "Maangu" tourmaline. During the examination of the "Maangu" tourmaline, various types of inclusions were identified, including trichites, two-phase inclusions, and solid crystals. These inclusions exhibited changes following the heat treatment process. The tiny trichites fully melted as the temperature increased. Additionally, vapors and fluid inclusions evaporated with the elevated temperature. In certain cases, cavities within the tourmaline were filled with melted liquid inclusions.

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