



# Identification of the Effect of Localization on the Colour Alteration of “Geuda” Gemstones Through the Heat Treatment Using ED-XRF, FTIR, and UV-Vis Spectroscopic Analysis

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## ABSTRACT

Over 75% of the gem-bearing gravels in Sri Lanka belong to the corundum species of gemstones. Geuda is a low-quality form of corundum, and it is abundant in most gem-enriched regions in Sri Lanka. It can be heat treated to transfer into worthy blue sapphires where the value alters with the degree of colour. However, the degree of colour enhancement is uneven in Geuda stones even if the heat treatment is conducted under the same conditions. Thus, this study focuses on evaluating the effect of localization on the colour enhancement of the milky Geuda variety. Fifty Geuda samples were collected from five gem-bearing localities in Sri Lanka; Ratnapura, Ridiyagama, Okkampitiya, Bakamuna, and Katharagama. These samples were washed and sonicated with dil. HNO<sub>3</sub> acid and faceted to have parallel smooth surfaces. Then all samples were observed and analyzed under a microscope, ED-XRF, FTIR, and UV-Vis spectroscopies and heated up to 1800 °C temperature for 60 minutes of the soaking period under reducing conditions. Then the analyses except XRF were repeated (before and after the heat treatment). Microscopic observations support visually identifying the degree of colour enhancement and inclusions changes. UV-Vis spectrums identified the cause of blue colour enhancement as the intervalence charge transfer (IVCT) developed by Fe<sup>2+</sup> and Ti<sup>4+</sup> ions, and the change in the degree of colour enhancement was also verified as an alteration in the degree of IVCT by the available ions. FTIR spectrum characterized the bond vibrational changes with the heat treatment, and FTIR was clarified as the best method to identify heat-treated blue sapphires since a characteristic peak was generated at 3310 cm<sup>-1</sup> after treatment. Apart from Ti and Fe, V was also determined to affect blue colour enhancement by ED-XRF analysis. The optimum blue colour was enhanced in the ratios of 1: 3: 323 for Ti: Fe: Al. there were significant changes in the location and ternary diagrams are accompanied to record the highest Ti content in Ridiyagama and the highest Fe content in Bakamuna and Katharagama. Furthermore, corresponding unique elemental ratios for these localities were encountered.

## 1. Introduction

Sri Lanka has had an excellent reputation for its high-quality gems since the early historic periods. The history of the Sri Lankan gems can be traced to almost 3000 years ago. The earliest explorers in Europe, Arabia, and Asia have written much about gems in Sri Lanka (Zwaan, 1982). The most common gem varieties in Sri Lanka are corundum (Ruby and

Sapphire), Garnet, Tourmaline, Spinel, Beryl, Quartz, and Topaz. Among these, Sri Lankan blue sapphire is the most expensive and famous gemstone type in the world (Dissanayake et al., 2000). Blue sapphire is a corundum (Al<sub>2</sub>O<sub>3</sub>) variety where the α-Al<sub>2</sub>O<sub>3</sub> crystallises in the trigonal crystal system. Here each Al<sup>3+</sup> ion is bonded to 6 oxygen ions in octahedral [AlO<sub>6</sub>]<sup>9-</sup> co-ordination. About 80% of Sapphires



found in Sri Lanka belong to low-quality Sapphires known as Geuda. Geuda is a low-quality form of corundum mineral which consists of semi-transparent to semi-translucent, whitish, semi-brownish, milky, or silky appearance in transmitted light due to  $\text{TiO}_2$  (Rutile) inclusions, with a characteristic “Diesel Effect” (colour of diesel fuel) due to  $\text{Fe}_2\text{O}_3$  (Soysa and Fernando, 1992; Rupasinghe et al., 1993). Their quality could be enhanced to resemble fine gemstones like ruby and sapphires by heat treatment.

### 1.1. Origin of Blue Color in Blue Sapphires

Corundum is generally colourless in its “pure” form. The blue colour of sapphire originates from inter valence charge transfer (IVCT) between  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  ions (Ferguson and Fielding, 1971; Fritsch and Rossman, 1987). If two adjacent octahedral sites are containing  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  instead of  $\text{Al}^{3+}$  in the corundum crystal structure, the outer orbital of both these ions overlaps with each other since the distance between  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  is relatively small (2.65 Å), and this configuration allows electrons to pass from one ion to the other (Nassau, 1983; Jaliya et al., 2019).

This process requires energy and exposure to white light that triggers an electron transfer from  $\text{Fe}^{2+}$  ion to  $\text{Ti}^{4+}$  ion, changing their valence states to  $\text{Fe}^{3+}$  and  $\text{Ti}^{3+}$  and facilitating selective absorption of incident white light producing a blue colour.



In addition to the transition described in the above reaction, charge transfer from

$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+}$  in the red region of the visible spectrum can also be attributed to accomplishing the blue colour.

### 1.2. Geological Setting of Corundum Gem Deposits of Sri Lanka

Geologically, Sri Lanka is dominated by Precambrian high-grade metamorphic rocks and can be divided into three major lithotectonic units: The Highland Complex, the Vijayan Complex, and the Wannai Complex (Cooray, 1994). Sri Lankan gem deposits are classified based on the genesis as (i). Metamorphic, (ii). Sedimentary and (iii). Magmatic (Dissanayake and Rupasinghe, 1995). Metamorphic gem deposits are the most common gem deposit type in Sri Lanka since about 90% of the land is underlain by high-grade metamorphic rocks. Gems created by metamorphism are mainly confined to the high-grade metamorphic terrain of the Highland Complex and are formed by skarn reactions (Rupasinghe et al., 1994). The majority of skarn-type gem deposits, such as corundum-bearing deposits located at Bakamuna near the Elahera area, were formed under granulite facies metamorphism (De Maesschalck and Oen, 1989). Because of the high abundance of aluminous metasedimentary rocks and favourable P-T conditions, most of the aluminous gem varieties can be observed in Highland Complex (HC).

Further, the genesis of these gemstones is related to granulite facies metamorphism, involving  $\text{CO}_2$  flooding and purging of  $\text{H}_2\text{O}$ -rich fluids (Katz, 1986). Gem deposits under magmatic type are mostly related to the pegmatitic origin and are common in the Highland Complex. These deposits are also

considered to be an essential source of corundum gem minerals (Rupasinghe et al., 1994). Sedimentary deposits are broadly classified into three types residual, eluvial, and alluvial deposits. Alluvial type gem deposits are the widely distributed gem deposit type in Sri Lanka, containing two or three gem-bearing layers occurring as old stream terraces and flood plains (Dahanayake et al., 1980). The regions such as Awissawella, Ratnapura, Rakwana, Balangoda, Bakamuna, Okkampitiya, Elahera, Ridiyagama, and Katharagama have undoubtedly supported to expose corundum bearing gem pits in Sri Lanka for several decades (Dissanayake and Rupasinghe, 1995). Among them, a considerable amount of Geuda varieties are heat-treated locally in Ratnapura and Beruwala.

### 1.3. Geuda Heat Treatment

Currently, heat treatment is carried out for various Geuda varieties. Among these, milky Geuda takes a prominent place which yields blue sapphires when undergoing standard treatment conditions. Milky Geuda's name is implied by its “milky” appearance (Pemadasa, 1993). There are some critical factors to be considered during heat treatment; the maximum temperature reached during treatment, the time for which the maximum temperature was sustained (commonly known as the soaking period), the rate of heating/cooling, and the atmospheric conditions inside the furnace (reduced, oxidized or inert) (Peiris, 1993). Furthermore, the chemical nature of the Geuda may influence the colour alteration mainly due to impurity amount changes.

All the milky Geuda gems received from various localities in Sri Lanka are heat-treated under the same conditions. Nevertheless, the blue colour enhancement of this milky Geuda is not equal as expected. Hence there is an essential requirement to investigate the reason for this colour variation. Therefore, the study focused on determining the effect of localization on the colour alteration of “Geuda” due to impurity changes.

## 2. Material and Experimental Procedure

Fifty Geuda samples (ten from one location) were selected from five gem-bearing regions in Sri Lanka; Ratnapura, Ridiyagama, Okkampitiya, Bakamuna, and Katharagama. Samples were coded as RT, RG, OP, BK, and KG, respectively, and washed with pure water. The two opposing sides of the cleaned samples were faceted and polished using the Imashi facetter to have parallel smooth surfaces. Again, the samples were thoroughly washed with pure water and sonicated with diluted nitric acid, washed again with distilled water, and prepared in such a way that they can be subjected to the analysis. Then, all milky Geuda samples were heat-treated with a maximum temperature of 1800 °C by the gas-fired heat treatment furnace (Lakmini furnace) for 60 minutes of the soaking period under reducing conditions. Previous studies (Pemadasa, 1993) and current industrial practices were considered in deciding the heat treatment conditions. Gemological Institute of America (GIA) colour grading system was used to categorize the heat-treated samples based on their tone, revealing the gem's lightness or darkness. The corresponding GIA colour grading codes for the collected samples are shown in Table 1.

2.1. Characterization

The colour and clarity of all Geuda samples were observed with a KSW8000 gemological microscope (A. KRUSS Optronic GmbH) under 40X magnification. The cause of colour was identified using an absorption spectrum under

UV-VIS spectroscope (MULTISKAN GO). Furthermore, Gemmo FTIR was used to verify the heat-treated milky Geuda by considering the changes in IR absorption. ED-XRF (Rigaku) was used to determine the elements of Geuda percentage-wise.

Table 1. The GIA Colour Grading Codes for the collected samples

Light Blue Colour Samples		Medium Blue Colour Samples		Dark Blue Colour Samples	
Sample No	GIA Colour Grading Code	Sample No	GIA Colour Grading Code	Sample No	GIA Colour Grading Code
RT001	B2/2	RT004	vB5/3	RT003	vB6/4
RT002	vB3/4	RT009	vB4/6	RT007	B7/4
RT005	B3/3	RG001	B5/5	RT008	B7/4
RT006	B3/3	RG003	vB5/5	RT010	bV7/4
RG002	B3/3	RG010	vB5/3	RG007	bV8/3
RG004	vB4/3	RG011	bV5/4	RG008	vB7/5
RG005	B3/3	OP001	vB4/6	RG009	B7/3
RG006	B2/3	OP003	vB5/3	OP002	B7/4
OP007	B3/4	OP005	B4/4	OP004	vB8/3
OP008	B2/2	OP006	vB5/4	OP009	B7/4
OP010	B3/4	BK003	vB4/4	OP011	vB7/3
BK001	B3/3	BK006	vB5/4	BK004	bV8/3
BK002	B2/2	BK007	vB5/3	BK009	vB7/3
BK005	B2/2	BK010	B4/5	BK011	B7/4
BK008	vB2/3	KG002	B5/3	KG006	vB7/3
BK012	B2/2	KG009	bV5/5	KG007	vB7/3
KG001	B3/2				
KG003	B3/4				
KG004	B3/4				
KG005	B2/2				
KG008	B3/3				

Table 3. UV-Vis absorption peak positions of Geuda gemstone

Peak position (nm)	Corresponding element/s	References
388	Fe <sup>3+</sup>	Smith et al., 1995; Schwarz et al., 2008
450	Fe <sup>3+</sup>	Smith et al., 1995; Schwarz et al., 2008
A broad absorption peak around 570	Fe <sup>2+</sup> /Ti <sup>4+</sup>	Ferguson and Fielding, 1971; Moon and Philips, 1994

3. Results and Discussion

3.1. Microscopic Observation

Table 1 shows an overview of the microscopic observations for representative five samples from five localities mentioned above.

Microscopic observations reveal an overall colour enhancement after heat treatment at 1800 °C for a 1-hour soaking period in a reduced environment. The observed results showed that the colour enhancement is proportionately increased with the concentration of the milky appearance. The clarity and transparency of 50 samples have increased due to dissolve of Titanium dioxide in corundum at temperatures above 1500 °C which complies with previous studies (Peiris, 1993). However, in some specimen's fractures have been developed or enhanced after heat treatment. The expansion of inclusions within the sample has a significant effect on the development of fractures. Furthermore, there is a significant alteration related to the inclusions of the sample's correspondence with the locality. Microscopic observations between Ridiyagama samples and Katharagama samples explain this (Table 2) since the number of inclusions and fractures in Ridiyagama Geuda

samples are comparatively less compared to Katharagama Geuda samples.

3.2. UV-Vis Spectrometry

Geuda samples initially do not reflect a blue colour since Ti and Fe are included as Anatase and Hematite as micro mineral impurities (Jaliya et al., 2020). Heating above 1500 °C tends to release Ti<sup>4+</sup> ions to the corundum structure by dissolving Rutile. Further, heat treatment in a reduced environment favours the reduction of Fe<sup>3+</sup> (in the form of Hematite) into Fe<sup>2+</sup>. Thus, the formed Fe<sup>2+</sup> and Ti<sup>4+</sup> replace two adjacent Al<sup>3+</sup> ions in the corundum structure. Hence, the blue colour is formed by creating an IVCT between the produced Fe<sup>2+</sup> and Ti<sup>4+</sup> ions (Peiris, 1993; Ileperuma, 1993).

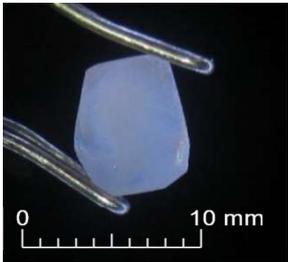
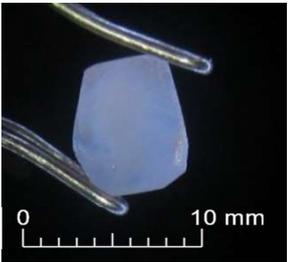
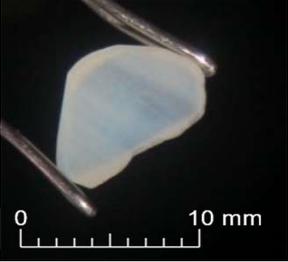
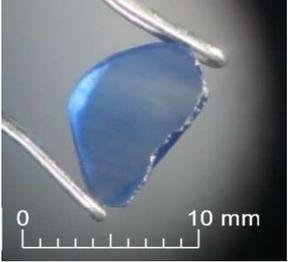
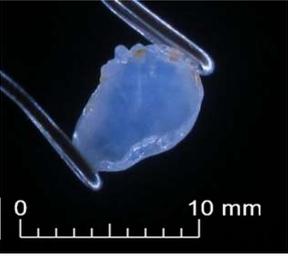
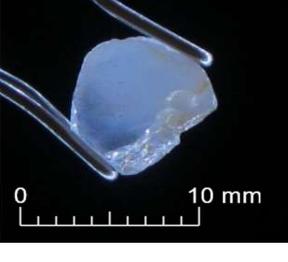
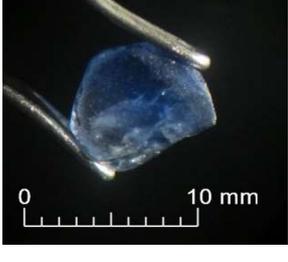
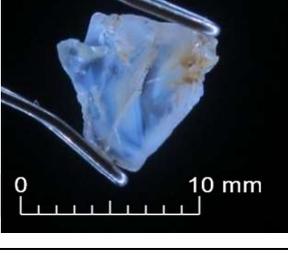
This study reveals the colour enhancement of Geuda through the identification of its relevant absorption peak alterations due to heat treatment (Table 3).

According to the results of the UV-Vis spectrum (Fig. 1), almost all the samples (before heat treatment) have established their characteristic peaks at 388 nm and 450 nm to represent the presence of Fe<sup>3+</sup> ions, whereas the absence of

the 570 nm peak addressed the unavailability of IVCT by  $[\text{FeTi}]^{6+}$ . The heat treatment process decreased the 388 nm and 450 nm peaks and enhanced a broad absorption peak around 570 nm representing the transformation of  $\text{Fe}^{3+}$  into

$\text{Fe}^{2+}$  ions and forming of  $\text{Ti}^{4+}$  ions by dissolving Rutile within the stone, which means the heating process has supported generating IVCT and verify the blue colour enhancement of the Geuda stones (Nassau, 1997).

Table 2. Microscopic observations of the selected samples from each locality

Unheated	Heated	Locality
		Ratnapura
		Ridiyagama
		Okkampitiya
		Bakamuna
		Katharagama

Furthermore, overall analyses of UV-Vis spectrums in five localities show the retention of a peak at 388 nm after heat treatment, which suggests excess  $\text{Fe}^{3+}$  (Perera and Gunasekera, 1993). This particular observation is significant for the region of Bakamuna samples (Fig. 1d)

**3.3. FTIR analysis**

During Fourier Transform Infrared spectroscopy analysis, the following absorption bands were identified (Table 4). Before and after heat treatment, FTIR spectrum analyses indicate characteristic variations concerning the peaks.

Almost all the samples showed an absorption band at 2342 or 2362  $\text{cm}^{-1}$  (Fig. 2). The peak at 2342 and 2362  $\text{cm}^{-1}$  correspond to atmospheric  $\text{CO}_2$  or  $\text{CO}_2$  gas trapped inside the

gemstones (as gas bubbles, two/three-phase inclusions, due to high-temperature heat treatment in reducing environment or as negative crystals) (Catier, 2009).

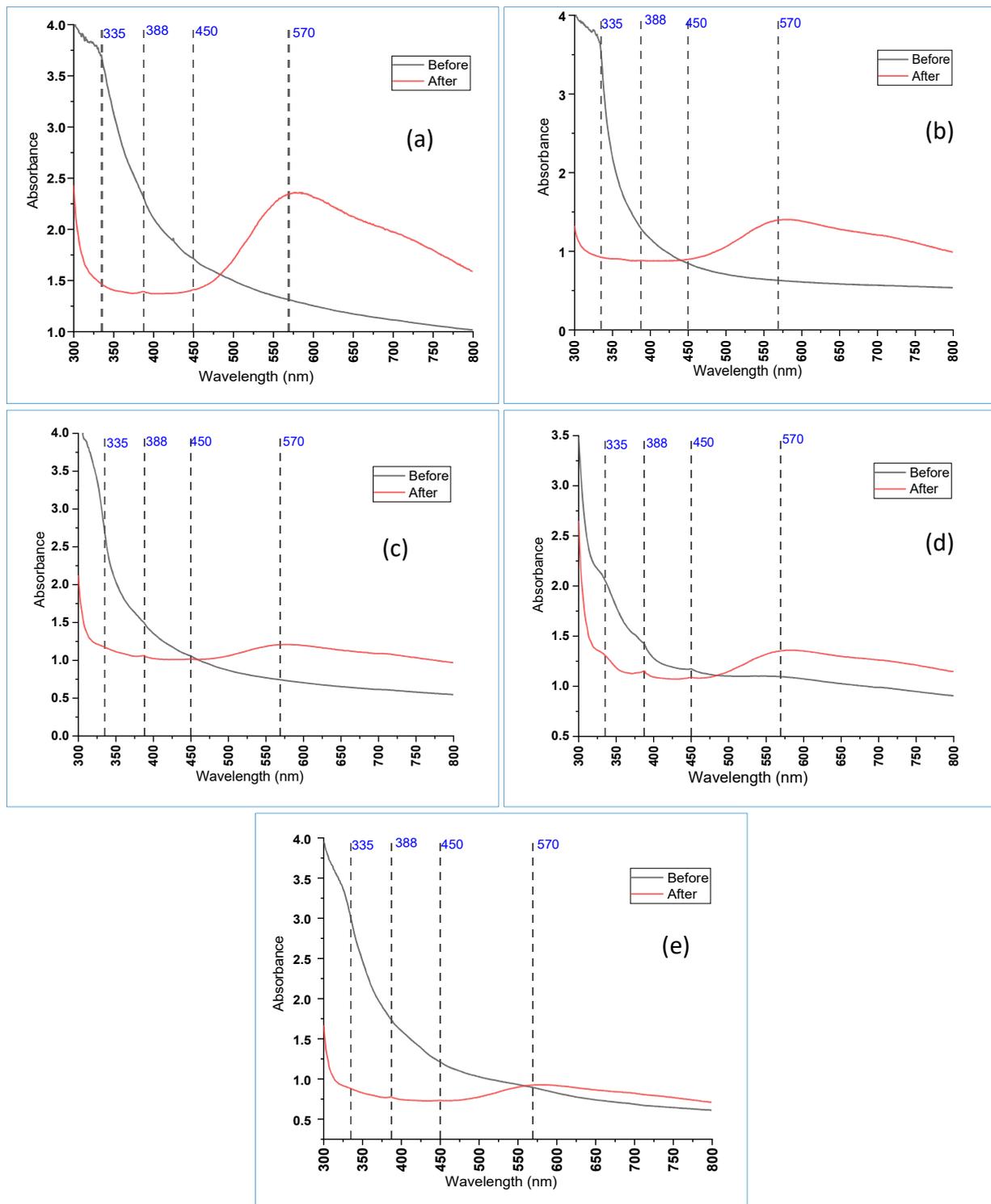


Fig. 1. UV-Vis Analyses of the samples (a) Ratnapura (b) Ridiyagama (c) Okkampitiya (d) Bakamuna (e) Katharagama

However, the  $\text{CO}_2$  peak in Geuda samples, not due to atmospheric  $\text{CO}_2$ , is inferred by  $\text{CO}_2$  trapped inside the crystal and confirmed by the correlation of a particular peak (before and after heat treatment) for every sample. The study utilized the 'Lakmini' gas furnace, which employs a combination of

liquid petroleum gas (LPG) and oxygen to generate the necessary reducing environment. Moreover, the heating process applied in the research reached a temperature of approximately 1800  $^{\circ}\text{C}$ , which may have led to the trapped  $\text{CO}_2$  in the Geuda specimens.

Table 4. The FTIR absorption band positions (cm-1) of Geuda gemstones

Absorption band (cm <sup>-1</sup> )	Relevant bond type	References
Sharp bands at 3185, 3233, 3310 and 3367	O-H in the corundum lattice	Beran, 1991; Emmett et al., 2003
Broadband around 3400	H <sub>2</sub> O	Smith, 1995
The sharp band at 3620, 3652, 3669 and 3697	Kaolinite	Smith et al., 2016
2342 and 2362	CO <sub>2</sub>	Catier, 2009
Band around 2853 and 2924	C-H as oil and fat	Catier, 2009; Geiger et al., 2009

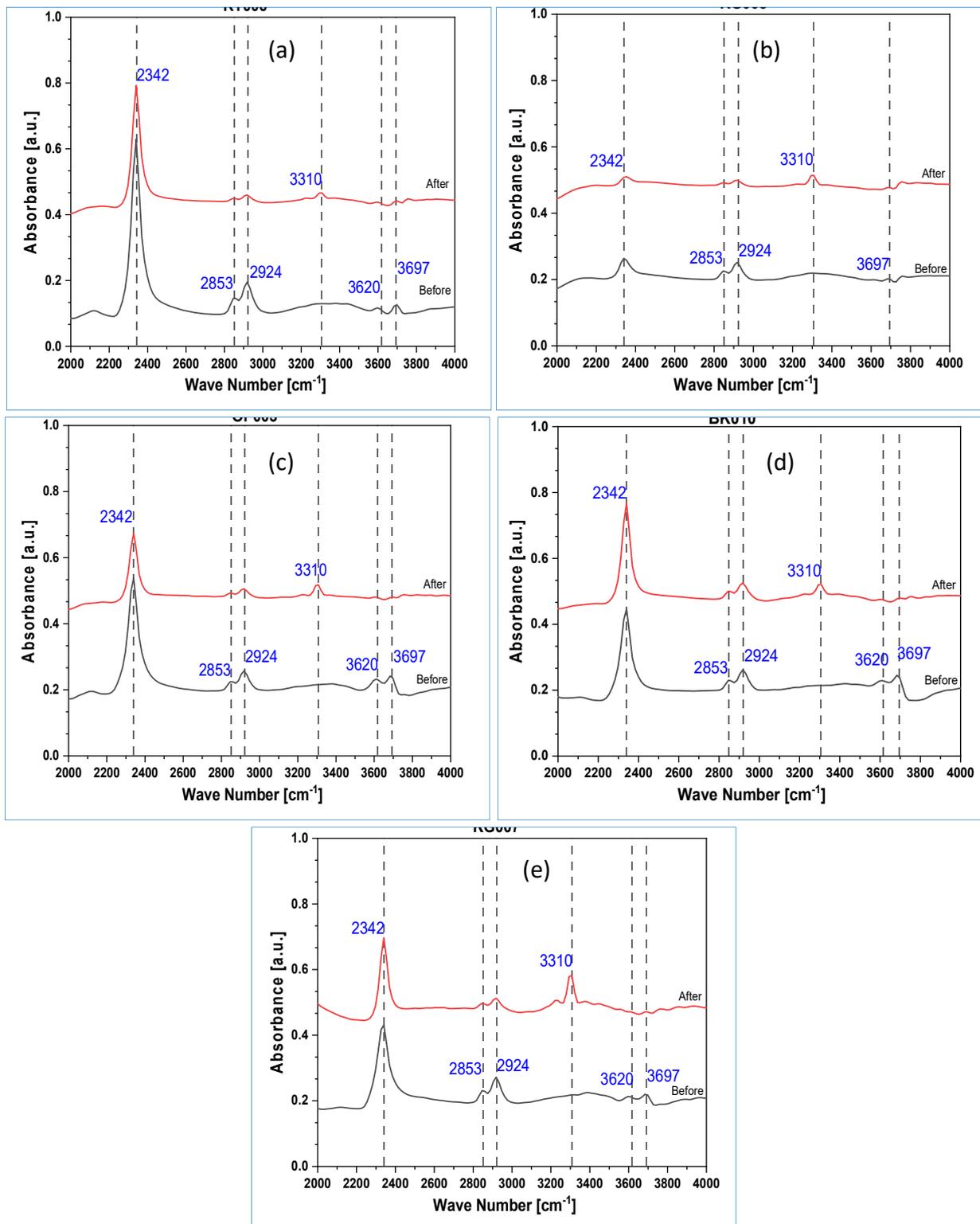


Fig. 2. FTIR Spectral Analyses of the samples (a) Ratnapura (b) Ridiyagama (c) Okkampitiya (d) Bakamuna (e) Katharagama

Table 5. Average percentage values of Al and trace elements (Fe, Ti, V)

	Al (%)	Fe (%)	Ti (%)	V (%)
Light	92.3556	0.7494	0.1858	0.0147
Medium	91.0833	0.9465	0.2817	0.0181
Dark	89.2938	1.0242	0.4166	0.0267

Furthermore, this particular peak's intensity is significantly less for Ridiyagama samples (Fig. 2 (b)) concerning other localities. That means the Ridiyagama samples have fewer CO<sub>2</sub>-trapped inclusions. Hence, FTIR analysis further clarifies the microscopic observations (Table 2) regarding the inclusions.

Additionally, the samples (before and after heat treatment) showed two peaks at 2853 and 2924 cm<sup>-1</sup> due to the C-H bond, which results from contamination of oil and fat (Geiger, 2004; Catier, 2009). Further, the O-H bond vibration peak corresponded to the 3400 cm<sup>-1</sup> (Smith et al., 1995), and the peak disappeared with heating, introducing another sharp absorption band at 3310 cm<sup>-1</sup> concerning an interstitial O-H bond in the corundum crystal structure (Beran, 1991). Since the heat treatments were carried out in a gas furnace, the atmospheric Hydrogen will diffuse back into the crystal and appear in the absorption spectrum as O-H, with the absorption features enumerated in the above spectrums as previously established (Emmett et al., 2003).

Furthermore, there were four absorption bands at 3620, 3652, 3669, and 3697 cm<sup>-1</sup> that correspond to Kaolinite hydrous mineral inclusions (Smith et al., 1995). Among them, 3620 and 3697 cm<sup>-1</sup> absorption band positions were identified with the collected Geuda samples before heating. Since the samples have been already sonicated with dil. HNO<sub>3</sub> acid (during sample preparation), the resulting peaks are not relevant to the surface-coated kaolinite. Thus, this might be due to hydrous kaolinite inclusions inside the specimens, and the identified bands have also disappeared on heating. FTIR and microscopic analyses together accomplish a significant correlation. With the increase of absorption intensity for CO<sub>2</sub> and Kaolinite, the stone tends to crack after heat treatment.

### 3.4. XRF Analysis

Analysis of the percentages of Al, Fe, Ti and, V (Table 5) provided a powerful platform for the study. The average percentage values of these elements provide a comprehensive idea of the localization effect.

Element percentages were obtained using Rigaku NEXCG, Energy Dispersive X-Ray Fluorescence Spectroscopy mode. Diaphragm size was 20 mm and analysed under a Helium atmosphere. XRF results depict and confirm that Al, Fe, Ti, and V have affected the colour enhancement of Geuda stones. Among them, the main colouring elements, Fe and Ti, which contribute to IVCT, have a proportionately pronounced effect on colour enhancement. Furthermore, the percentage of V also contributed to producing dark blue (Table 5). Furthermore, a detailed study on ratios of average percentages for the corresponding light, medium, and dark colour stones provides a deep understanding of the behaviour of main colour-causing agents (Table 6).

The increase of Fe content concerning Ti has retarded the colour enhancement, which means when the stone shift from light to dark, the concentration of Ti plays a crucial role in determining the degree of blue colouration in sapphires, which is consistent with the fact that the dissolution of Ti with Fe, produces [FeTi]<sup>6+</sup> complex is responsible for the blue hue. Most of the examined Geuda possess an excess of Fe, which implies that the Ti will predominantly bind with Fe following dissolution into the corundum lattice. Therefore, Fe is unlikely to be the primary factor influencing colour in these specimens. The role of Fe in colouration would only be significant if the amount of Fe present were insufficient to offset the dissolution of Ti into the corundum lattice.

Table 6. Average ratios regarding Ti, Fe, and Al elements

	Ti	:	Fe	:	Al
Light	1	:	4	:	497
Medium	1	:	3	:	323
Dark	1	:	2	:	214

Moreover, a comparative analysis of the average percentage value ratios of Ti, Fe, and V accomplishes a significant correlation to the localization (Table 7). A crucial increment in Ti compared to Fe content has resulted in a better colour enhancement of stones from Ridiyagama. Nevertheless, Bakamuna and Katharagama samples have shifted towards higher Fe content, confirming the highest Fe-bearing regions among the above localities. V: Fe ratios also discriminate a significant association to bring a unique identity to the corresponding locality. V compared to Fe is significantly high in Ridiyagama, Okkampitiya, and Ratnapura, respectively. Fe content compared to V is continued to be high in Bakamuna and Katharagama regions.

Table 7. Elemental ratios and the corresponding sample locality

Sample location	Ti : Fe	V : Fe
Ratnapura	1 : 2.6	1 : 30.4
Ridiyagma	1 : 1.5	1 : 28.1
Bakamuna	1 : 5.1	1 : 63.4
Okkampitiya	1 : 2.5	1 : 29.4
Katharagama	1 : 5.2	1 : 76.6

Thus, a specific technical card can be proposed to identify and verify the specific locality of the acquired data.

1. Technical card ratio values for Ti: Fe are shown below;

- 1 : 1.2 to 1 : 1.8 → Ridiyagama
- 1 : 2.2 to 1 : 2.9 → Ratnapura or Okkampitiya
- 1 : 4.8 to 1 : 5.5 → Bakamuna or Katharagama

2. Technical card ratio values for V: Fe are shown below;

- 1 : 15 to 1 : 45 → Ratnapura, Ridiyagama, Okkampitiya
- 1 : 50 to 1 : 80 → Bakamuna or Katharagama

#### 4. Conclusion

Microscopic photographs and spectral investigation of fifty Geuda samples from five gem-bearing localities in Sri Lanka indicate that the Ridiyagama area samples have fewer inclusions than other localities. The expansion of existing inclusions has been the reason behind the development of fractures after heat treatment. UV-Vis spectral analysis suggests that the creation of IVCT is the responsible factor for blue colour enhancement for milky Geuda. Furthermore, the milkiness appearance affects the development of IVCT. FTIR spectrum analysis reveals that Ridiyagama corundum exists with fewer CO<sub>2</sub> trapped inclusions due to its peak intensities (2342 and 2362 cm<sup>-1</sup>) before and after heat treatment.

Furthermore, a characteristic FTIR peak was enhanced at 3310 cm<sup>-1</sup> in all the samples after heat treatment. Retention of absorption bands at 3620 and 3697 cm<sup>-1</sup> was identified as non-heat-treated blue sapphires. However, all non-heat-treated blue sapphires may not show the considered peaks. Thus, FTIR spectral analysis may be recommended to distinguish heat-treated blue sapphires from their natural ones.

XRF analyses provide evidence that Fe is sufficiently present in almost all corundum varieties. However, Ti content is comparatively less. Therefore, the degree of IVCT formation is administered by limited Ti content. Hence, Ti content can be identified as the dominant element that affects colour enhancement. Detailed analysis of XRF results suggests the average ratio of 1: 3: 323 for respective Ti, Fe, and Al elements as the ideal ratio to obtain optimum blue colour in Geuda.

Furthermore, a detailed analysis of elemental ratios identified a significant increase in Fe content in the Bakamuna area and increased Ti content for the Ridiyagama area's corundum. This significant fluctuation of elements enables generating a unique ratio to identify the specific locality. Thus, it is confirmed that the origin of the Geuda has a pronounced effect on the colour enhancement of Geuda through heat treatment.

Finally, ED-XRF is the most unique and sophisticated method to investigate the colour enhancement and origin of milky Geuda gemstones compared to other analytical techniques. Furthermore, Ridiyagama can be introduced as the most appropriate locality to select Geuda stones for heat treatment in the other four regions in Sri Lanka. Hence, it opens new avenues for the Sri Lankan gem dealers during decisive instances, which may indirectly affect the overall benefit and prosperity of the Sri Lankan economy.

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