Characterization of zircons in Buttaia - Okkampitiya gem fields,Sri Lanka: An implication for heat treatment

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Declaration

The work described in this thesis was carried out by me at the Faculty of Applied Sciences, under the supervision of Asst. Prof. Dr. Pomsawat Wathanakul and Prof. Mahinda Rupasinghe. A report on this has not been submitted to any other university for another degree.

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Abstract

Zircon is considered as a low quality gemstone, with various colour varieties, which is used to traditional heat treatment by Buttala - Okkampitiya gem traders for enhancing its quality and colour. Yellow and pastal green varieties are commonly found in the study area. The green varieties are different from Ratnapura green zircons and the yellow zircons found from the study area are with high radioactivity and consists inclusions that are unique to green zircons. The characteristics such as specific gravity, radioactivity, reflectivity, surface and internal features of zircon samples from heavy mineral concentrates were studied using hydrostatic balance, geiger muller counter, reflectometer, microscope and Visible light spectroscope, UV-VIS-NIR, FTIR and EDXRF techniques. Samples were heat-treated using electric furnace.

Heat treatment resulted the yellow and violet zircons to transform into colourless under 800 \degree C for 2 hrs in oxidation condition, which can be used as a substitute for diamond by their adamantine luster. Under less oxygen condition green zircons become bluish colour. According to the results, yellow zircons show metamict characteristics. The different Zr/Hf ratios from EDXRF indicating the zircons are from different origins. These results can be used as a base for comparison of other gem varieties and as a base for cost effective zircon enhancement.

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Chapter 3 Regional Setting

Chapter 4 Materials and Methods

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A bbreviations used in the text

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

List of Figures

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List of Tables

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Chapter 1 Introduction

1.1 General Introduction

Gemstones are enhanced by scientific and traditional methods. The upgraded properties after the enhancement make the gemstones more valuable. Gem is an exhaustible resource and remaining quantities of gems are reduced with the extraction. This will result the low quality gems to become more valuable in future. In nature all the gem varieties are not found in a better quality to use as gems. Therefore gem enhancement methods are becoming a popular industry. Gemstone enhancement was not very familiar in the Sri Lankan gem industry. During the decades of 1970s and 1980s the lack of knowledge of heat treatment of geuda lost millions of foreign exchange to the country. In Sri Lanka the enhancement is only done by the experience. This may sometimes leads to failure of the process. Therefore people are more doubtful in gemstone enhancement.

Zircon is a commonly found heavy mineral in the heavy mineral concentrate and considered as low quality gemstone. There are many colour varieties of zircons namely, green, yellow, violet, brown, red, orange and colourless etc. Especially green variety is used as a substitution for emerald, as emerald is not found in Sri Lanka Therefore the green variety has a good market and relatively good price. According to Gubelin and Koivula (1992) the green metamict zircon is almost exclusively to Sri Lanka The colourless zircon is used as a substitution for diamond as zircon has an adamantine luster (Rupasinghe and Senaratne, 1986).

Buttala - Okkampitiya gem field is one of the main gem bearing areas in Sri Lanka. All most all the gem varieties, which are found in Sri Lanka, are found in this particular gem field. Green to yellow colour varieties is prominently found in Buttala - Okkampitiya gem field. Though green zircons found in the particular gem field frequently the green colour is not as bright as Ratnapura. Because of that the demand for Buttala - Okkampitiya pastel green variety is lower than Ratnapura bright green variety. Colour of the Zircon in the Buttala -Okkampitiya gem field is enhanced by the local gem miners and traders using their own heating techniques. Burning coconut husks is a traditional method used in enhancement of colour. Because zircon is having more colour variations and all most all the varieties show changes of colour by heat treatment, the identification of characteristics of these varieties, before heat treatment will be more useful to predict the colour change.

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1.2 Prior Studies

Many researches have been carried out on zircons and the enhancement of them through out the world, for more than one hundred years. But only few studies have been done on Sri Lankan zircons. Vitanage (1957) had studied the types of zircons in pegmatites, gneisses and quartzite of Ceylon Precambrian complex. A study of an orange metamict zircon has done by Anderson (1961) and Vance and Anderson (1972) has done research on low Ceylon zircons showing radiation damages. Textural and morphological studies of zircons from the crystalline rocks of the Precambrian Vijayan complex of Sri Lanka has been done by Weerasooriya et al., (1983). Rupasinghe and Senaratne (1986) have studied about improving quality and colour of zircons. They have used 1000 $^{\circ}$ C, 15 hours, both oxidation and reduction conditions, rapid cooling and slow cooling methods. The geochemistry and mineralogy of zircons from the stream sediments and rock samples in Ratnapura and Ellahera gem fields of Sri Lanka studied by Rupasinghe and Dissanayake (1987). Baur et al., (1991) have studied the U- Pb isotopic systematics of zircons from prograde and retrograde transition zones in high- grade orthogneisses of Sri Lanka.

1.3 Scope of the Study

There are only few scientific studies done on the study area. Therefore the characterization of zircon in the particular gem field is studied. Most frequently found zircons are yellow and green. The green variety in the study area is having dull colour. The yellows are used to heat treatment by traditional methods. The conditions for heat treatment and change of colour by heat treatment of zircons in Buttala - Okkampitiya gem field is useful to find a cost effective method of zircon enhancement. The only scientific method for enhancement of the colour of zircons is tried by Rupasinghe and Senaratne (1986) using both oxidation and reducing conditions with very high temperatures around $1000⁰C$ and for a long time (15 hrs), which is not cost effective. Characteristics of Buttala - Okkampitiya zircons are identified and compared with some zircons from Ratnapura gem field and some from Thailand.

The main objectives of the study are,

- Identification of characteristics of zircons in Buttala Okkampitiya gem field > ¥ — *
- Identification of condition for heat treatment
- Identification of colour change after heat treatment

Chapter 2 The Mineral Zircon

The name zircon is very old and is believed to be derived from the Arabic *zarqun,* in turn derived from Persian *zar,* gold, and *gun,* colour. Zircon is a widely distributed accessory mineral in granitic and syenitic igneous rocks; it is a fairly common detrital mineral in some sediments and it is also found in metamorphic rocks. Well-crystallized varieties, both clear and coloured, have long being used as gemstones (Deer et al., 1997).

2.1 Mineralogy of Zircon

2.1.1 Crystallography

Klein and Hurlbut (1993) describe the crystallography as the study of crystalline solids and the principles that govern their growth, external shape and internal structure. When external form is considered zircon crystallizes in the tetragonal system and the crystals take the form of combination of square prism terminated at either end by a square pyramid or a combination of pyramids (Figure 2.1).

Figure 2.1 Zircon crystals

2.1.2 Physical Properties

2.1.2.1 Cleavage

Cleavage is tendency of mineral to break parallel to atomic planes that are identified by Miller indices, just as the faces of the external form of the crystal (Klein and Hurlbut, 1993). The zircon cleavage is said to be imperfect in $\{110\}$ (direction of prism) and poor in $\{111\}$ (parallel to pyramids).

2.1.2.2 Hardness

The resistance that a smooth surface of a mineral offers to scratch is its hardness. The Mohs scale of hardness introduced by Friedrich Mohs is still in use to express the hardness of minerals. The hardness of the zircon is 7.5 in Mohs scale.

2.1.2.3 Colour

The colour is the property, which can be observed first and most easily. Zircons show wide range of colours varying from colourless, through yellow, red, orange, brown and yellowishgreen, a bright of leaf green to dark green. Colour of zircons depends on the trace elements and radiation damages.

2.1.2.4 Lustre

Luster is the general appearance of a mineral surface in reflected light. Zircon has an adamantine luster that is exceptionally brilliant luster like that of a diamond, due to its high refraction index.

2.1.2.5. Specific gravity

Specific gravity (S.G) is the number that expresses the ratio between the weight of a substance and the weight of an equal volume of water at $4⁰C$. On the basis of specific gravity, there are high, low and intermediate grade zircons. Specific gravity of zircons varies from $3.9 - 4.71$, low to high types.

2.1.3 Optical Properties

2.1.3.1 Refractive Index

Refractive Index (RI), n, of a mineral is the ratio between the velocity of light in air (V_a) and its velocity in the mineral (V_m) , that is,

o

$$
\mathbf{n} = \mathbf{V_a} / \mathbf{V_m}
$$

The RI of zircon is higher and it varies with type of zircon, which is mostly based on the specific gravity. According to the Read (1991), the RI s of zircons are,

2.1.3.2 Optical Indicatrix

The optical indicatrix is the geometrical shape relating the RI of a mineral to die mineral structure. The surface of the indicatrix represents the different refractive indices in the crystal. These different refractive indices are related to the different vibration directions that linearly polarized light can vibrate parallel to while in mineral.

As zircon crystallizes in the tetragonal system it is anisotropic uniaxial positive and doubly refractive in optical characters (Figure 2.2). That is it processes two perpendicular refractive indices ordinary (ω) and extraordinary (ϵ) . The uniaxial indicatrix is an ellipsoid and positive or prolate means that extraordinary ray is greater than die ordinary ray.

Figure 2.2 Optical Indicatrix of uniaxial positive crystal.

2.1.3.3 Birefringence

The birefringence is the difference between the highest and the lowest refractive indices. It is said that birefringence of zircon is inversely proportional to the intensity of radioactivity (Table 2.1).

Table 2.1 Birefringence of different types of zircons (after Deer et al., 1997).

2.1.4 Chemical Composition and Structure

Zircon is an orthosilicate mineral having the chemical composition of ZrSi**04** - zirconium silicate, in which the content Of $ZrO₂$ is 67.2% and SiO₂ is 32.8%. Zircon always contains some Hafnium (Hf). Zirconium (Zr) can substitute with Hf because of the dose similarity in their chemistry. Zr is in 8- coordination with oxygen in the form of distorted cube like polyhedra. The eight oxygen belong to six different SiO₄ tetrahedra (Figure 2.3). Although the structure of zircon is resistant to normal chemical attack, it is often in a metamict state. This is caused by the structural damage from Th and U present in small amount in many zircons (Klein and Hurlbut, 1993).

The colour of zircon depends on the accessory element composition. The different colour varieties have different trace elemental concentrations. The green zircons are relatively enriched with Hf, Th and U whereas the rose and violet varieties show low Hf, Th and U concentrations. The green variety has the lowest Zr/Hf ratio of 33, and violet type the highest ratio of 48. Further the green zircon exhibit the lowest Zr/Th and Zr/U ratios in contrast to the rose and violet types (Rupasinghe and Dissanayake, 1987).

- Figure 2.3 (a)The structue of zircon reviewed along x, showing chains of alternating edgesharing SiO₄ tetrahedra and ZrO₈ triangular dodecahedra extending parallel to z and laterally by edge-sharing dodecahedra
	- (b)The structure of zircon, showing chains of altering edge- sharing SiC**>4** tetrahedra and ZrOg dodecahedra projected on (001) and showing the edge- sharing between dodecahedra (Dear at el., 1997).

2.2 Mineralization and the occurrence of zircon

Porldvaart (1956), in summerizing work on zircon concentrates from igneous rocks, showed that the crystallization of zircon is late in the consolidation of basaltic magma, early in dioritic or granitic magma, and may be early or late in alkaline rocks.

Zircon is a common accessory mineral of igneous rocks. As zircon is relatively resistance to erosion it is a common accessory mineral in many sediments. In metamorphic rocks zircon is less common but may be found in orthogneiss even after regional metamorphism (Deer et al., 1997).

2.3 Zircons and their radioactivity

Many zircons contain Th and/or U as the trace elements. The self-irradiation from the decay of U and Th produces the zircon radioactive and metamict. The radioactivity depends on the concentration of U and Th. As the colour of a mineral is affected by its chemical composition and different colour varieties have different elemental concentrations. Colour of zircon is an indicator to its degree of radioactivity. The green varieties show the highest degree of radioactivity whereas violet shows the lowest (Rupasinghe and Dissanayake, 1987).

2.3.1 Metamict State

Minerals describe as metamict are originally formed as crystalline solid, but their crystal structure has been destroyed, to various degrees, by radiation from radioactive elements present in the original structure (Klein and Hurlbut, 1993).

It is believed that the structural breakdown results mainly from the bombardment of alpha (α) particles emitted from the radioactive U and Th contain in the zircon (Klein and Hurlbut, 1993). With each alpha emission the emitting nucleus recoils displacing lattice atoms (Figure 2.4) (Deer et al., 1997).

Figure 2.4 (A) An alpha particle formed from the spontaneous decay of U or Th approaches a stable portion of a mineral where atoms are bound together

(B) The energetic alpha particle colloids with atoms of the structure causing displacements and structural damages (Deer et al, 1973).

Figure 2.5 shows several stages of destruction of the original crystal structure of zircon owing the presence of radioactive U and Th. Stage (a) shows a well ordered structure with well establish periodicities throughout; this is the unaltered structure. Stage I (b) shows some destruction of the structure and appearance of some aperiodic domains. Stage II shows large increases in the volume percentage of amorphous domains as a result of further destruction of the structure. In the final stage, III, all periodicities of the origial structure are lacking and material is totally amorphous (Klein and Hurlbut, 1993). With the metamictization density falls by 16% (Dear et al., 1997). Some of the optical properties such as birefringence and refractive index may change with the metamictization.

Figure 2.5 Schematic representation of the progressive damage done to the structure of zircon as a result of radioactive decay. Electron diffraction patterns and/ or X-ray diffraction patterns can be used to establish the amount of structural damage (Klein and Hurlbut, 1993).

2.4 Heat Treatment of Zircon

Zircons from Cambodia are well known for the heat treatment throughout the world. Reddish brown zircon from Cambodia can be transformed to die more popular blue colour by heating it to around 1000 ^oC in a reducing atmosphere. Although this is regarded as a permanent change, the intensity of the resulting colour can fade slowly over a period of time if exposed to strong sunlight (Read, 1991).

According to Read (1991), if reddish brown zircons are heated to around 900 °C in air, their colour can be changed in to colourless, golden brown or red. Some low and intermediate type zircons, whose crystal structure have been damaged by alpha particles emitted from isomorphous traces of uranium and/or thorium, can be lightened in colour (and their SG and RI values raised towards that of high zircon) by heating them to 1450 °C for around 6 hours. This causes the near amorphous silica and zirconia produced as a result of the alpha-particle irradiation to recombine as crystalline zircon.

Heat treatment of zircons is done in Sri Lanka using traditional methods and indigenous knowledge using coconut husks.

Chapter 3

Regional Setting

Sri Lanka is a tropical island, which lies within the 5^0 54'- 9^0 52' North latitudes and 79⁰ 39'-81⁰ 53' East longitudes and 32 km to the east of the southernmost extremity of Indian peninsula. It has an area of 65610 km^2 and is 432 km long and 224 km wide.

3.1 General Geology of Sri Lanka

Precambrian (Proterozoic) crystalline rocks underlie Nine tenths of the island, the rest being made up chiefly of Miocene limestone in the North and northwest coastal regions. The Precambrian is subdivided into 3 main and one subordinate lithotectonic units (Cooray, 1994) (Figure 3.1). They are Highland Complex (HC), Wanni Complex (WC) Vijayan Complex (VC), and Kadugannawa Complex (KC).

3.1.1 Highland Complex (HC)

The HC consists of about 50% of metasedimentary rocks and 50% of metaigneous gneisses (Kroner et al., 1991). The most obvious metasediments are marble, orthoquartzite and metapelite. Minor constituents are caicsilicate rocks, either at the contact between marble and adjacent lithologies or as boundaries within marble or orthoquartzite, sapphirine- bearing highly magnesiam granulites have now been recognized in three localities (Kriegsman, 1993). These rocks are metamorphosed under upper amphibolite to granulite facies.

3.1.2 Wanni Complex (WC)

The WC consists predominantly of metaigneous gneisses and metasediments. The metaigneous gneisses generally have granitic, granodioritic and tonalitic composition. Metasediments include gamet-silimanite gneisses, often with cordierite, caicsilicate layers and possibly some grey gneisses containing small garnets.

3.1.3 Vijayan Complex (VC)

The VC consists of metaigneous gneisses of leucogranitic to tonalitic composition (Kröner et al., 1991) with rare inclusions of metaquartzite and caicsilicate rocks (Dahanayake and Jayasena, 1983). The mineral content is variable, but the most common minerals are quartz,

plagioclase, biotite, amphibole and K-feldspar. The geochemical characteristics of this granitoid suite that they are I-type intrusions.

Much of the structural history of VC is comparable to that of HC but the two units are of completely different origins, brought together by thrusting. Within the VC tectonic klippen of HC rocks as at Kataragama and Buttala (Cooray, 1995).

3.1.4 Kadugannawa Complex (KC)

Rocks of the KC are exposed in the cores of six double plunging D3 synforms and one intervening antiform in the Kandy area (Vitanage, 1972, Munasinghe and Dissanayake, 1980) and structurally overlie the gneisses of HC. The main rock types are biotite-homblende and biotite gneisses with amphibolites and minor metasediments of quartzo-feldspathic, quartzitic and pelilic composition (Vitanage, 1972; Perera, 1983; Cooray, 1984; Kröner et al., 1991).

3.2 Physiography and Geology of the study area

The Buttala-Okkampitiya gem fields are situated within the Buttala klippe, covering approximately 125 km² of the area.

3.2.1 Physiography of the study area

The climate of the study area is relatively dry. The most prominent morphological feature of the Okkampitiya area is an erosional remnant, which occurs in the form of a 'Turtle Back' hill. The rest of the area is generally flat and gently undulating (Mathavan et al., 2000). The Kumbukkan Oya is the only perennial river runs through the study area. Other than that several seasonal streams can be seen during the rainy season. The tributaries of Kumbukkan Oya drain from the upper areas in the North and then enter into the broad, flat and gently undulating Okkampitiya area in the South and Southeast.

3.2.2 Geology of the study area

Geological studies have shown that the combined HC-WC unit was over thrust on to the VC, and isolated remnants of HC rocks occur as 'klippen' or 'outliers' within the VC region. The Buttala Klippe, which is found near the HC-VC boundary but in the area of VC, is one such occurrence (Kroner et al., 1991). Buttala klippen is surrounded by VC rocks and may be either large remnants of the HC that escaped deformation and restoration to form VC gneisses or thrust klippe (Cooray, 1984). Although the critical contact between the Buttala klippe and the VC masked and obliterated by superficial deposits, recent mapping clearly show a zones of mylonite between the two complexes, suggesting that the complexes have been juxtaposed by thrusting associated with deep seated tectonic collision (GSMB Moneragala - panama sheet 18, 2002).

The study area is underlain by marble, pelitic gneisses, quartzite, migmatite, basic granulite, minor pegmatites and calcsilicate rocks. Marble is the dominant lithology within the Okkampitiya region. Though marble is mainly composed with calcite and dolomite, other minerals such as diopside, phlogophite, spinel and forsterite are also present in minor amount (Mathavan et al., 2000). During the field visits an insitu zircon deposit was discovered. In the deposit two colours of zircons are found. They are honey brown and violet.

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Chapter 4

Materials and Methods

4.1 Sample Collection

Zircons from the river gravels, which are alluvial, elluvial or residual were collected for die characterization of zircons of Buttala - Okkampitiya gem fields, Sri Lanka. The number of samples collected is 260.

4.1.1 Zircon Samples in the Gem -bearing Gravel Layer

Zircon is a common gem mineral found within die river gravels of Buttala- Okkampitiya gem field. The river gravel containing gems is named as 'Illama' in Sinhala. After the panning of gem bearing gravel layer and selecting the valuable gems the remaining heavy mineral concentrate is called as the 'Nambuwa'. The 'Nambuwa' samples collected by the workers of the mines were carefully examined and the zircons were handpicked. As the zircon is a less valuable gem compared to die other gems such as the corundum Zircons less than 5 carats could be found in the 'Nambuwa'. Attempt was made for collecting maximum number of coloured varieties. The samples were collected from six locations in the Buttala - Okkampitiya area (Figure 4.1).

4.2 Sample Description

Under the sun light samples were separated into six major colours namely green, yellow, violet, brown, opaque and off colour. Some of the major colours were grouped into subclasses such as dark- green, green, light-green, greenish- yellow, dark- yellow, yellow, lightyellow, greenish- brown, light violet and violet. Altogether there are thirteen sub classes of colours (Figure 4.2).

Out of the various groups, 56 samples were selected as representatives for studying. For the comparison six-zircon samples of dark green, light green, dark yellow, light yellow, brown $\frac{1}{2}$ and violet from the Ratnapura gem fields and the three reddish brown zircons from Thailand were also taken (Figure 4.3, Figure 4.4). The weight in carats, specific gravity, colour and the surface feature of the sample representatives are studied for the sample registration (Appendix 1).

Figure 4.1 The sampling locations in the study area (after GSMB Moneraguia -

Panama sheet 18, 2000) o 2 4 km

Legend

- 1 Granite gneiss
- 2 Biotite hornblend migmatite
3 Biotite gneiss
-
- 4 Marble
5 Walawe
- Walawe gneiss
- 3 Biotite gneiss **Sampling locations**
4 Marble

Figure 4.2 Thirteen groups of zircon samples of different colours from Buttala- Okkampitiya Sri lanka

Figure 4.3 Zircon samples from Figure 4.4 Zircon samples from Ratnapura Thailand

4.3 Sample Preparation

The experiments were earned out at the Earth Sciences, Dept, of General Sciences. Faculty of Science, Kasetsart University, Bangkok, Thailand and Gem and Jewellary Institute of Thailand. Thailand.

The weight, specific gravity, and surface features could be measured in the rough samples. For other measurements such as colour, identification of internal features, reflectivity and especially for the spectroscopy (UV-VIS-NIR) the samples were polished. For UV-VIS-NIR characterization, the UV ray should pass through the C axis of the mineral. As the \hat{C} axis does not scatter plane polanzed light C axis shows the darkest in the plane polarized light.

The Polariscope, which consists of two polar, the lower one is the polarizer, which transmits the light vibrating North-South, and the upper one. analyzer that transmits the light vibrating East-West and is used to analyze the C axis (Figure 4.5). When minimum light passes through the two polars. it is said to be crossed. Under the condition of crossed polars the C axis of the samples were marked. And the samples were polished according to the C axis. The weights as well as the thicknesses of the samples were again measured after the polishing.

Figure 4.5 The Polariscope Figure 4.6 Hydrostatic balance

4.4 Basic Characteristic Measurements of Zircon Samples

4.4.1 Weight and Specific Gravity Measurements

The weight and the specific gravity of the samples were measured using the hydrostatic balance (Figure 4.6). The weight unit considered here are carats. The formula used to calculate the specific gravity (S.G) is,

$$
S.G = \frac{Weight in Air}{(Weight in Air - Weight in Water)}
$$
 x Temperature Correction Factor

4.4.2 Hardness

Hardness of the zircon samples was measured using the hardness pencils. Hardness pencils have been prepared according to the minerals of Moh's scale.

4.4.3 Surface Features

The surface features of the zircon samples were observed under the microscope (Figure 4.7) at the magnification of 10X and to inspect the features further magnification of 40X was used.

Figure 4.7 The microscope used for identification of internal and surface features

4.4.4 Colour

The colours of the stones were identified using Gemmological Institute of America (GIA) colour set (Figure 4.8) under the standard light of colour stone grading lamp (SOW/ 220- 230V). The zircon sample and the reference colour stick were hold about 10 cm under the standard light and compared (Figure 4.9).

Figure 4.8 Portable GIA colour set Figure 4.9 Comparing colours

4.4.5 Reflectivity

Zircon is having a high refractive index, which cannot be measured by the scale of the normal gem Refractometer. Because of that reflectivity of the zircon samples were measured. According to Read (1991) the reflectivity is the ratio between the intensity of the reflected ray and that of the incident ray. One of a polished surface was mounted on the Reflectometer and the read the digital number appeared on the window and compared with the table of reflectivity in the instrument (Figure 4.10).

4.4.6 Visible Light Spectrum

The spectroscope was used to the identification of observation spectra of zircon samples. The diffraction grating (diffractive dispersion) type of spectroscope (Figure 4.11) was used. The scale of the spectroscope was a non- linear scale. The observed spectrum lines were drawn on a paper. The line spectra of all the samples of colour groups were observed and marked.

Figure 4.10 Reflectometer Figure 4.11 Diffraction grating spectroscope

4.4.7 Internal features

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Internal features were observed after polishing. The microscope (Figure 4.7) was used to study the inclusion and internal features under the magnification of 40X and 60X.

4.4.8 Radioactivity

The radioactivity of the samples verses weight was measured using the Geiger Mueller Counter (Figure 4.12). The unit taken is total count per minute. The sample was placed on the desk and the sensor of the instrument was placed about 1cm above the sample. Two measurements were taken, inside a room where other mineral samples are also stored and outside the room. The radioactivity was calculated for one gram of sample.

4.5 Advance Spectroscopic Characterization

4.5.1 Ultra Violet -Visible -Near Infra Red (UV-VIS-NIR) Spectrometer

The absorption of the energy in the ultra violet to near infrared wavelength region by the zircons of different colour groups were examined using the UY-VIS NIR (Model Lambda 900) Spectrometer (Figure 4.13).

Some selected samples from the six major colour groups were used for the inspection of the spectrum. The C axis of the sample is used to measure the spectrum that is E ray spectrum of the sample was inspected. The detector and monocromator were adjusted at 750 nm wavelength as there was no recognizable peaks of the zircon absorption spectrum. The integration times were 0.04 s and 0.08 s for UY-VIS and NIR respectively.

Figure 4.13 The UV-VIS-NIR Spectrophotometer Figure 4.12 The Geiger

Mueller Counter

4.5.2 Fourier Transform Infra Red (FTIR) Spectrometer

The Nicolet FTIR spectrometer (Model NEXUS 470) was used for the examination of the transmission spectra in the infrared region of the zircons (Figure 4.14). For the IR spectrum inspection also the selected representatives out of 65 representatives selected from each colour group were used. The number of sample and background scan was 64.

Figure 4.14 The FTIR Spectrophotometer

4.6 Chemical Composition

4.6.1 Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer

EDXRF model ED 2000 (Figure 4.15) was used for the analysis of chemical composition of the zircons of various colours. Some samples out of the 65 selected zircons taken as representatives of each colour group and analyzed.

Figure 4.15 The Energy Dispersive X-ray Fluorescence Spectrometer

4.7 Heat Treatment of zircon

Two main conditions were suggested for heat treatment experiment of the samples, Oxidation and Reduction. The oxidation experiment for pilot samples done according to two methods,

- 1) Closed crucible (less oxygen), temperature 800° C and 2 hours and temperature 1000° C, for I hour.
- 2) Open crucible (more oxygen), temperature 800° C and 2 hours.

For the reducing condition same temperature and time is applied without oxygen. Lenton Furnaces is used for oxidizing heat treatment.

First, pilot zircon samples were used for selecting the condition for heat treatment. The pilot sample in the open crucible was sent to heat treatment in the reducing condition 800 $^{\circ}$ C, 1 hour. According to the results from pilot samples a sample group was selected and heattreated under reducing condition, 800 °C, 1 hour.

Chapter 5 **Results and Discussion**

5.1 Properties of zircons of Buttala - Okkampitiya

5.1.1 Surface Features

Shape of the zircon can be described mainly as rounded, irregular and crystals. Out of 36 samples around 40% are remained as crystals while 35% are in irregular shape and other 25% are rounded (Figure 5.1).

Opaque zircon crystal

Rounded greenish brown zircon

Irregular shaped yellow zircon Figure 5.1. Morphology of zircons under the magnification of 10X

Under the magnification of 10X, the surfaces of nearly fifty percent of the samples contain pinhole nature and little damages such as broken edges. The samples of the violet group contain fewer damages on their surfaces. All the other groups contain higher damages. There damages are clearly observed at a magnification of 40X. Those are with fractures and cracks (Figure 5.2).

 $10X$ 40X

A sample (SBB01) with a fractured surface under the magnification of 10X and 40X

A sample with fracture on the surface 10X (SBG02)

A sample with damage edge 40X (SBGY3)

A sample with pinhole nature A sample with little damage and little damages (SBLG4) (SBV02)

Figure 5.2. Surface features of the samples

As the zircon is not a very hard mineral compared to corundum (hardness is around $6.5 - 7.5$) during the transportation it can be rounded and at the same time cracks, fractures and break down of edges can occur. The hardness of the samples is shown in figure 5.3. The Opaque with black colour has its crystal shape remained and subjected to fewer damages. But it has a relatively low hardness of around six, which means that it has not been transported long distance and close to their place of origin. The violet and off colour to colourless samples have the highest hardness among other zircon samples. As the off colour samples are rounded, they may have transported a long distance away from their place of origin. The violets have remain the crystal faces and with less damage. So they may not be transported a long distance. But they have a higher hardness than the opaque. Therefore it can be said that they have been transported a long distance than the opaques. As the green, brown and yellowsamples are rounded they may have transported a long distance away from the original sources.

Figure 5.3 The hardness of zircons of Buttala

5.1.2 Specific Gravity

The Specific Gravity (S.G) of zircon is in the range of 4.0 to 4.9. When they are grouped into colours and plotted against Specific Gravity, there is an observable relationship between the colour and the Specific Gravity (Figure 5.4). The opaque and the green varieties show a relatively low value of Specific Gravity. Yellow, brown and greenish brown zircon lie on the intermediate range. Violet and off colour varieties show relatively higher S.G. values than the others.

Figure 5.4. Specific Gravity of zircons of Buttala.

The results can be interpreted as following,

 $4.0 - 4.4$ \longrightarrow Opaque and Green zircons

 $4.3 - 4.6$ Yellow and Brown and Greenish brown zircon

 $4.5 - 4.9$ \rightarrow Violet and Off colour

Though there is no any clear demarcation of Specific Gravity values with the colours, the results implies a correlation between colour and the Specific Gravity. Therefore factors causing the colour could effect on the Specific Gravity.

5.1.3 Reflectivity

The reflectivity of zircons of Buttala is same as general zircon mineral and it lies in a range between 35 to 55. The green and opaque zircons give relatively low reflectivity, where as yellow, brown, greenish brown and violet and Off Colour show a relatively high reflectivity. The results are plotted in the scatter plot considering the colour (Figure 5.5).

Figure 5.5 Reflectivity of zircons of Buttala

The different coloured groups possess different reflectivity values. The elements cause to colour may affect on the reflectivity. The reflectivity depends on the surface where the light reflects. Therefore the fractures or any particle present on the reflective surface also affect the results.

5.1.4 Internal features

Zircon plays a rather minor role as host to inclusions, although it is remarkable as a guest mineral in many gems from various sources. Ocurrences of some crystal or solid inclusions in zircons of study area are found (Figure 5.6). Some zircons are with internal cracks (Figure 5.7) and in some cases the cracks are filled with guest minerals (Figure 5.7). According to Gübelin and Koivula (1992) in the high and medium zircons, the guest minerals are limited to few fantastically patterned cracks, iron stains are also present as an internal feature of some zircons of Buttala-Okkampitiya gem field (Figure 5.8). some zircons especially the violets contain the growth zones (Figure 5.9).

Figure 5.6 Crystal inclusion in Zircon (SBCL6) 60X

Figure 5.8 Iron stain in zircon (SBDG1) 40X

Figure 5.7 Crack filling in zircon (SBB01) 60X

Figure 5.9 Zoning in a violet zircon (SBDG1) 40X

Metamict zircon inclusions have caused typically fine fissures and tension halos in many gemstones as a result of such volume increase. The green zircon is limited almost exclusively to Sri Lanka. Of all colours, the green metamict zircon is the only variety known to date, which has proven fruitful in inclusion investigation. Without any further tests, the green metamict zircon is usually easy to identify by its inclusion scene (Gübelin and Koivula, 1992).

The "finger print" inclusions can be resulted from tension fracturing and subsequent healing in zircon. This is observed in some samples of green and yellow zircons (Figure 5.10). The burst fissures or disc shaped tension feature is also observed in some green zircons (Figure 5.11). This feature is characteristic feature of Sn Lankan green zircon, which results from the radiation induced destruction of the zircon lattice. Another unmistakable feature of the green metamict zircon from Sri Lanka is the consistency of parallel stripes resulting from metamictization, which is also observed, in some green zircon samples (Figure 5.12).

According to Gubelin and Koivula (1992) the angular tension fractures, which delineate the former tetragonal structure and are the only remnants of the original crystal structure are characteristic to metamict green zircons of Sri Lanka. But in zircons of Buttala -Okkampitiya gem fields this feature is recorded in two yellow zircon samples (Figure 5.13). The radioactivities of these zircons are almost the same as the green zircons in the particular study area. But the specific gravity and the reflectivity are little higher than the greens.

Figure 5.10 Finger print in zircon (SBG3) 40X

Figure 5.12 Parallel stripes in green zircon (SBGY4) 40X

Figure 5.11 Burst fissures in green zircon (SBLG3) 40X

Figure 5.13 Angular tension fractures in zircon (SBLY2) 40X

5.2 Radioactivity of zircons of Buttala

The radioactivity of the sample for 1 g of its weight is taken for comparison. The results are grouped in to colours. The opaque samples, which show the highest radioactivity, are black or dark brown. The two samples of opaque, which give the low radioactivity, are yellow to yellowish brown. The yellow samples are spread in a relatively large range of radioactivity. After opaque and yellow, the greens have the next comparatively high radioactivity. The off colour samples show the lowest radioactivity. Violet and brown samples lie in an intermediate range. The ranges are overlapped not well separated. The figure 5.14 shows the radioactivity measurements of the zircons of Buttala.

Figure 5.14 The radioactivity of zircons of Buttala

5.2.2 Correlation of Radioactivity with Specific Gravity and Reflectivity

The results of Specific Gravity indicate a negative relationship with radioactivity. Higher the radioactivity of the mineral lower is the Specific Gravity. The correlation coefficient of S. G. and radioactivity is —0.66. Not only with S. G., but the radioactivity shows a relationship with colour of the mineral. Therefore mineral colour and specific gravity can put together with the radioactivity of zircons (Figure 5.15).

The reflectivity of the zircon also changes with the radioactivity. With increasing radioactivity the reflectivity of the zircon decreases. The correlation coefficient of these two parameters is -0.43 shows a weak correlation in between these two. The colour of zircon can plot with the radioactivity and reflectivity (Figure 5.16).

The specific gravity and reflectivity of the zircon mineral vary not only with the small amount of iron and similar elements, which may enter the structure but also with the degree of alteration or metamictization. Variation in the cell dimensions of zircon due to metamictization have been reported by Holland and Gottfried (1955) and the obtained results indicating that the lattice expansion in metamict zircon is anisotropic with two a dimension, aj: a**2**, being 1.001 to 0.9735, while die c dimension also expands from 5.974 **A** for fresh material (S.G 4.66) to 6.080 **A** for metamict material (S.G 4.18) (Deer et al., 1997).

Figure 5.15 Relationship between radioactivity and specific gravity

Figure 5.15 Relationship between radioactivity and reflectivity

5.3 Spectroscopic Characteristics of zircons of Buttala - Okkampitiya

Spectroscopy refers to the investigation of spectra, the phenomena observed when the electromagnetic radiation from a source is separated into their constituent wave lengths correspond to the spectral colours. The absorption spectrum produced by a particular gemstone depends on its chemical composition. Frequently, the absorption spectrum of a gemstone is characteristic of minor elements present as colouring agents (Hurlbut and Kammerling, 1991).

5.3.1 Visible Light Spectroscopy

The dark lines of the visible light spectrum are created due to the absorption of the energy by the electrons of the elemental atoms. The observed absorption spectrums differ from colour group to colour group. In all the samples the violet region is completely dark and no absorption line of the spectrum is observed. The common absorption line of the spectrum, which appears in the all samples, lies between 650 nm and 660 nm. It appears darker than all other lines and they are weaker compared to that. The common spectrum appeared in-groups of dark green, green, light green according to the classification done is as in figure 5.17.

Figure 5.17 The common Spectrum for green zircon varieties.

The maximum number of spectrum lines are observed in sample SBLG2 (Figure 5.18). According to Flurlbut and Kammerling (1991) the cause of fuzzy absorption lines for green colour zircon is the presence of Uranium.

Figure 5.18 Absorption spectrum of zircon sample SBLG2.

The samples of greenish brown where show the spectrum of six lines (Figure 5.19). The yellow, light yellow and some samples (SBVOl, SBV02 and SBLV1) give the spectrum of only one fine (Figure 5.20). It is a line that lies around 650 nm. The sample SBLV2. a violet sample shows a spectrum of four lines (Figure 5.21).

nm

Figure 5.19 Absorption spectrum of sample group of greenish brown zircon.

Figure 5.20 Absorption spectrum of yellow zircons and some violet zircons.

Figure 5.21 Spectrum of some violet zircon samples

The other samples of light violet and violet groups and some samples of near to colourless to colourless group do not show any spectrum. The SBCL2. SBCL3 and SBCL5 samples of the off colour group give the spectrum of three lines (Figure 5.22).

Figure 5.22 Absorption spectrum of some off colour zircon samples

The absorption bands of the spectrum are determined by the elements present in the mineral. The different colours of the zircons may contain different trace elements. The occurrence of different trace element may cause the difference in spectrum.

5.3.2 UV- VIS- NIR Spectroscopy

UV -VIS -NIR measures the absorption spectrum in the energy region of Ultra Violet (UV) to infrared . Thse spectrums are particular for each mineral and with the colour of the same mineral. That is with the factors of colour of the minerals. Some absorption peaks like 1500 nm and 1113- 1117 nm are common to most of the colours. The greens and greenish brown zircons give large number of peaks in the visible region . The sharpness of the peaks depends on the quantitative characteristics. The UV- VIS- NIR spectra for different colour varieties are shown in Figure 5.23a to 5.23e.

Figure 5.23a The UV-VIS-NIR spectrum of green zircon (1.14 ct, E ray)

Figure 5.23b The UV-VIS- NIR spectrum of yellow zircon (1.3 ct, E ray)

Figure 5.23c The UV-VIS- NIR spectrum of Brown zircon (2.7 ct, E ray)

Figure 5.23d The UV-VIS- NIR spectrum of violet zircon (1.0 ct. E ray)

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Figure 5.23e The UV-VIS- NIR spectrum of colourless zircon (1.3 ct, E ray)

5.3.3 FTIR Spectroscopy

FTIR is for measuring the absorbtion spectrum of infrared (IR) region. The infrared spectra of zircon is well characterized in the $2000 - 4000$ cm⁻¹ range. While the spectra of natural zircons vary somewhat, all exhibit a broad transmission region between $2200 - 3100$ cm⁻¹. A strong absorption feature lie between $3100 - 3600$ cm⁻¹. The vriations of spectra are due to trace elements of the different coloured zircons. Figure 5.24a to Figure 5.24d show die differences of FTIR spectra among different colours.

Figure 5.24aThe FTIR spectrum of green zircon

Figure 5.24b The FTIR spectrum of yellow zircon

 \mathbf{r}

Figure 5.24c The FTIR spectrum of violet zircon

Figure 5.24d The FTIR spectrum of colourless zircon

5.4 Chemical Characteristics of zircons of Buttala -Okkampitiya

The chemical analysis of the major and minor components of the zircon samples are given in the table 5.1. When weight by percentages of Hf and Zr are plotted it shows an increasing of Hf content and, decreases the Zr content (Figure 5.25). Zr and Hf are very similar crustal incompatible elements and hence can be used to differentiate between different crustal proceses (Chandrajith et al., 1999). The value of Zr/Hf ratio in most crustal rocks lie close to 40 (Brooks, 1970; Murali et al,1983). In mid oceanic ridge basalt and oceanic island basalt, this ratio has been estimated to average $36.6 + -2.9$ (Jochum et al., 1986). However the Zr/Hf ratio is known to increase with increasing alkalinity (Pavlenko et al., 1957). And increasing degree of silica undersaturation (Dupuy et al., 1992). Eaqually high Zr/HF ratios have been observed in zircons from interplate alkali basalt and carbonatites (Zr/ Hf=52-81; Heaman et al., 1990), nephelene syenite $(Zr/Hf=-80$; Dupuy et al., 1990) and kimberlite pipes (Zr/Hf=58-65; Scharer et al., 1997). Though the Zr content is not much varied, the Hf content varies from 0.4 to 1 W% causing different Zr/Hf ratios.Therefore the occurrences of different ratios of Zr/ Hf precumbly provides evidence of different origins of zircon in Buttala-Okampitiya gem field.

Sample	SiO ₂	ZrO ₂	HfO ₂	Fe ₂ O ₃	Total	Colour
SBDGI	52.66	45.94	1.23	0.15	100	Green
SBG02	51.44	47.74	0.79	0.01	99.99	Green
SBLG4	44.83	54.63	0.49	0.03	100	Green
SBGY3	54.12	44.73	1.11	0.02	100	Yellow
SBY01	54.37	44.76	0.82	0.03	99.99	Yellow
SBGB3	48.35	50.59	0.99	0.05	100	Brown
SBLV4	41.67	57.74	0.50	0.07	99.99	Violet
SBLV2	53.33	45.70	0.94	0.01	99.99	Violet
SBV02	49.82	49.39	0.75	0.01	100	Violet
SBBO1	51.53	47.65	0.64	0.16	100	Yellow
SBO01	54.31	44.80	0.82	0.05	99.99	Opaque
SBO03	49.26	47.71	1.29	1.77	100	Opaque
SBCL2	50.27	49.01	0.68	0.01	100	Off colour
SRDG	46.17	52.91	0.88	0.02	100.00	Dark green
THRB2	52.97	46.09	0.91	0.02	100	Brown

Table 5.1 EDXRF results of zircons

Figure 5.25 Relationship of Zr/Hf ratios

5.5 Changes of zircons of Buttala Undergone Heat Treatment experiments

The samples which were heat treated under the 800 $\,^0C$, 2 hr in oxidation conditions (placed on the lit) show die colour changes as figure 5.26. The Samples were turned into pale colour after heat treatment. The green remains almost same. The colour of the opaque is also

changed. But it is not a better change of quality. After heat treatment the greenish brown turned to a translucent and dull colour.The violet and yellow loose their colours and turned into colourless.

Figure 5.26 Colours before and after heat treatment (800 \degree C, 2 hr, Oxidation)

After the heat treatment under oxidation condition the samples were heat treated under the reduction conditions, 800 °C , 1 hr aimng to recover the lost colours due to heat treatment under oxidation condition. Colour could not be recovered but the green zircon in the resulted sample turned to pale blue colour and zircons that became colourless turned into more colourless (Figure 5.27).

Figure 5.27 Comparison of colours before and after heat treatment under less oxy gen condition

In the less oxygen (closed crusible) condition under 800 $\,^0$ C and 2 hr soaking time, the green turn to pale blue colour. The greenish brown turned to a translucent and dull colour. The Opaque gives the brown colour like iron which is not good in economic manner. The violet and yellow have changed to little pale yellow colour. When these samples were heated again into 1000 °C ,1 hr at the same oxygen conditions green, greenish brown and opaque remained

same. Pale yellow colour obtained by the previous treatment has been turned to more lighter (Figure 5.28).

Figure 5.28 Comparison of colour before and after heat treatment under less Oxygen condition (a) Sample before the treatment (b) Sample in the crucible before the treatment (c) Sample after 800 \degree C, 2 hr heat treatment under less Oxygen condition (d) Sample after 1000 *° C ,* I hr heat treatment under less Oxygen condition

From the above experiments it was decided that 800 °C condition is enough for the heat treatment of zircon and less oxygen condition is useful for better change of colour. Therefore samples were treated under reduction condition for 1 hour soaking period. The results are given in the table 5.2 and Figure 5.29.

Table 5.2 Colour change after reduction condition

Before After

5.6 Comparison of zircons of the study area

For the comparison zircons from Ratnapura and Thailand were taken. The SRDB1, SRLG2. SRDY3, SRDG4, SRY05, SRV06 are zircons from Ratnapura, Sri Lanka and colours are brown, light green, dark yellow, dark green, yellow, violet respectively. THRB1, THRB2, THRB3 are brown colour zircons from Thailand.

The specific gravities of brown zircons of Buttala. Ratnapura and Thailand lie in the same range as the brown zircons of Buttala - Okkampitiya gem field. The specific gravities of the yellow, light green and violet lie in the same ranges as the yellow, green and violet zircons ot Buttala respectively. The dark green zircon (SRDG4) from Ratnapura is an exception. None of the green zircon was found at the Buttala - Okkampitiya gem fields similar to that colour (stg Y 7/3). The specific gravity of this zircon is 3.85.

When the reflectivity of the zircon samples are considered the brown in three locations are in the same range. SRDG4 shows the lowest reflectivity of 34 which deviates from the green zircon from Buttala.

The hardness of brown zircons of Thailand is little lower than the brown those in Sri Lanka. The Thailand and Ratnapura zircons taken for the analysis are not with many inclusions. Only observable inclusions found in these samples are fractures and cracks.

The dark green zircon from Ratnapura gives significantly higher value of radioactivity among other zircons. When comparing the three brown zircons the brown zircons give a slightly lower value of the radioactivity than the brown zircons from Buttala and Ratnapura Sri Lanka.

The absorption spectrum possessed by the yellow zircons from Ratnapura is similar to the yellow zircons of Buttala (Figure 5.19). The spectrums of two green zircon from Ratnapura are not so clear as green zircons of Buttala. but the spectrum line, which lies at the 650 - 660 nm is darker and clearer (Figure 5.30).

Figure 5.30 The spectrum of green zircon Ratnapura.

The brown zircon sample from Ratnapura shows the spectrum as in figure 5.31. The violet sample from Ratnapura does not show any spectra. Any spectrum line is not observed by the reddish brown zircons from Thailand.

Figure 5.3 1 The absorption spectrum of brown zircon from Ratnapura

The dark green sample of Ratnapura gives an exceptional UV-VIS-NIR spectrum (Figure 5.32). It contains less number of peaks than the Buttala- Okkampitiya green zircons. The UV-VIS-NIR spectra of the other colours are almost same. The UV-VIS- NIR spectrum of Thailand brown zircon contains no any significat peaks (Figure 5.33). Therefore the UV -VIS-

NIR spectrum of Thailand brown zircon is differ from the Buttala- Okkampitiya brown zircons.

Figure 5.32 The UV- VIS- NIR spectrum for Ratnapura dark green zircon

(6.8 ct, both E and O rays)

Chapter 6

Conclusion

Zircon is a commonly found heavy mineral which is considered as a low quality gemstone having various colour varieties such as green, yellow, violet, brown, red, orange, colourless etc. Buttala-Okkampitiya gem field is considered as a highly probable gem-bearing region. Here zircons are traditionally enhanced by heat treatment methods but there are only few scientific researches done about the gems in the particular study area. The commonly found zircons in the Buttala-Okkampitiya gem fields are yellow and green and the green zircons do not show the brightness of Ratnapura green zircons.

The various characteristics of zircons such as specific gravity, radioactivity, reflectivity, surface and internal features were studied using hydrostatic balance, geiger muller counter, reflectometer and microscope. Visible light spectroscope, UV-VIS-NIR, FTIR and EDXRF were also used to study the characteristics of zircons and samples were heat-treated using electric furnace.

The results from UV-VIS-NIR and FTIR prior to heat treatment readily show the characteristics of zircons. These results can be used to identify heat treatable zircons before heat treatment by comparing its characteristics with the results. The Visible light spectroscope is a simple instrument, which can be used by gem traders, in zircon identification with its unique bands and identification of heat treatable zircons. During the o heat treatment process the yellow and violet zircons transformed into colourless under 800 °C for 2 hrs in oxidation condition but the best results are given by the reduction heat treatment. Under 800 °C for 1 hr in reduction condition, yellow and violet zircons turned to colourless while green and greenish yellow turned to blue with the increase of luster.

The yellow zircons of the study area show high radioactivity closer to green variety and also comprised of inclusions that are characteristic to green zircons indicating metamict characters. The different Zr/Hf ratios from EDXRF indicating the zircons are from different origins. These results can be used as a base for comparison of other gem varieties and as a base for cost effective zircon enhancement.

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Appendix I

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