

CHAPTER 1

INTRODUCTION

Gem and jewelry business is one of the top ten of Thailand's export earners. In 2004, it ranked sixth with export value of US\$ 2,647.1 million (Ministry of Commerce Thailand, 2005). Corundum is an important gemstone in jewelry making, because of its beauty, hardness and durability. Corundum is discovered in many areas of the world, including Sri Lanka, Tanzania, Afghanistan, India, Australia, Cambodia, Laos, Myanmar and Thailand. At present, corundum produced from these areas have decreased dramatically. Madagascar, with the recently discovered new deposits, has become one of the most important gem-producing countries in the world. Since mid 1990's, quite a large volume of gem quality corundum has been mined in Madagascar (Schwarz and Schmetzer, 2001; Shida, 2002). In late 1998, large amount of corundum was discovered at Ilakaka, in southwestern Madagascar. Corundum from this area is pink, blue, violet, yellow, orange, green, pale brown and colourless (Milisenda and others, 2001). However, most corundums from this area need to be heat treated to enhance its quality and value.

The heat treatment process has still remained the treaters' experience and secret until today. Traditionally, the treaters tried to heat corundum through many trial-and-error processes. Most of the times, the process caused damage to the corundum. Only a few heat treatment processes of corundum, such as those from Sri Lanka, USA, Australia and Vietnam, were reported through publications (Emmett and Douthit, 1993; Pemadasa and Danapala, 1994; Themelis, 1995; Winotai and others, 2001). Since sapphires from Ilakaka are becoming more important as a new gem source and large quantities have been brought into the Thai market, the changes of sapphire after heating should be systematically studied, so that the heat treatment process can be appropriately controlled.

1.1 Geology of Ilakaka

Madagascar is the world's fourth largest island, located in the Indian Ocean. The size of this island is around 587,000 km². About 165 million years ago, Madagascar separated from the Gondwana supercontinent and drifted about 400 kilometers east into the Indian Ocean and halted there (Chikayama and Furuya, 2001). The Precambrian of Madagascar can be divided into central-northern sector and south-western sector which are separated by the main shear zone, Ranotsara Shear Zone. The central-northern sector is dominated by amphibolite to granulite facies, orthogneisses, migmatites and granites. The southern sector predominantly consists of rocks of high grade metamorphic paragneisses (Dissanayake and Chandrajith, 1999; Henn and Milisenda, 2001).

Western and south-western Madagascar is mainly occupied by the sedimentary Morandava basin, forms part of a larger basin which finds its continuation on the East African continent. The sediments in this basin were deposited continuously from Carboniferous times (about 345 Ma ago) to Tertiary times less than 60 Ma ago (Figure 1.1) (Henn and Milisenda, 2001; Milisenda and others, 2001).

Ilakaka is a village of Fianarantsoa province and situated 750 kilometers southwest of Antananarivo (the capital of Madagascar), and 215 kilometers northwest of Toliara on the west coast (Chikayama and Furuya, 2001). Since summer 1999 mining has been concentrated in three main areas. The first region, around the village of Ilakaka, includes a 90 X 20 km wide belt between Ranohira and Sakahara. The second area covers a 30 X 20 km wide zone around Fotiyola and Andranolava, south of Ankazoabo. The third area is Murarano (Figure 1.2) (Milisenda and others, 2001).

The discovered alluvial gemstone deposits in the south-western Madagascar, is recovered from sediments of the Isalo Group which consists of alternating sandstone and red argillitic layers. Mining is controlled by the Ministry of Mines. The miners hand dig pits in the weathered sediments to reach the productive gem-bearing conglomerate layers, which are loaded into sacks and taken to the nearby stream for washing (Laurs, 2000; Henn and Milisenda, 2001; Milisenda and others, 2001).

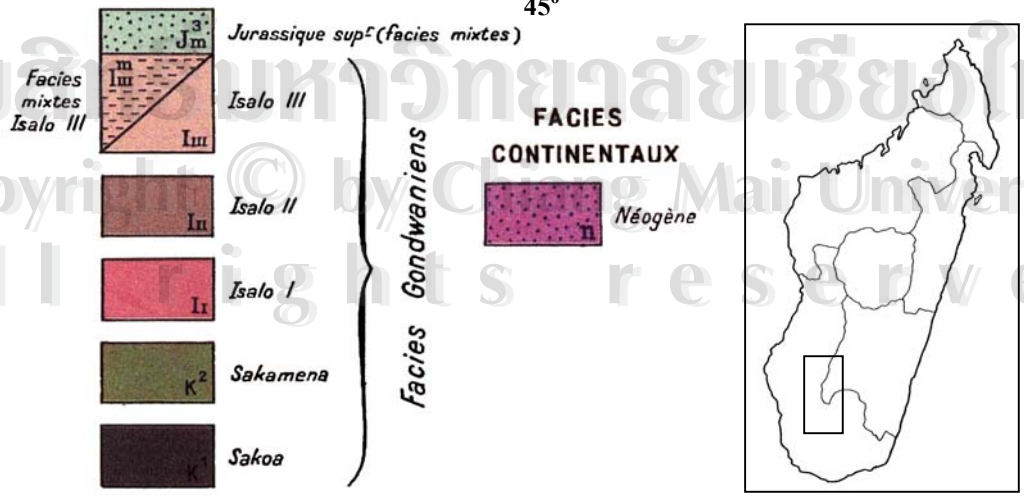
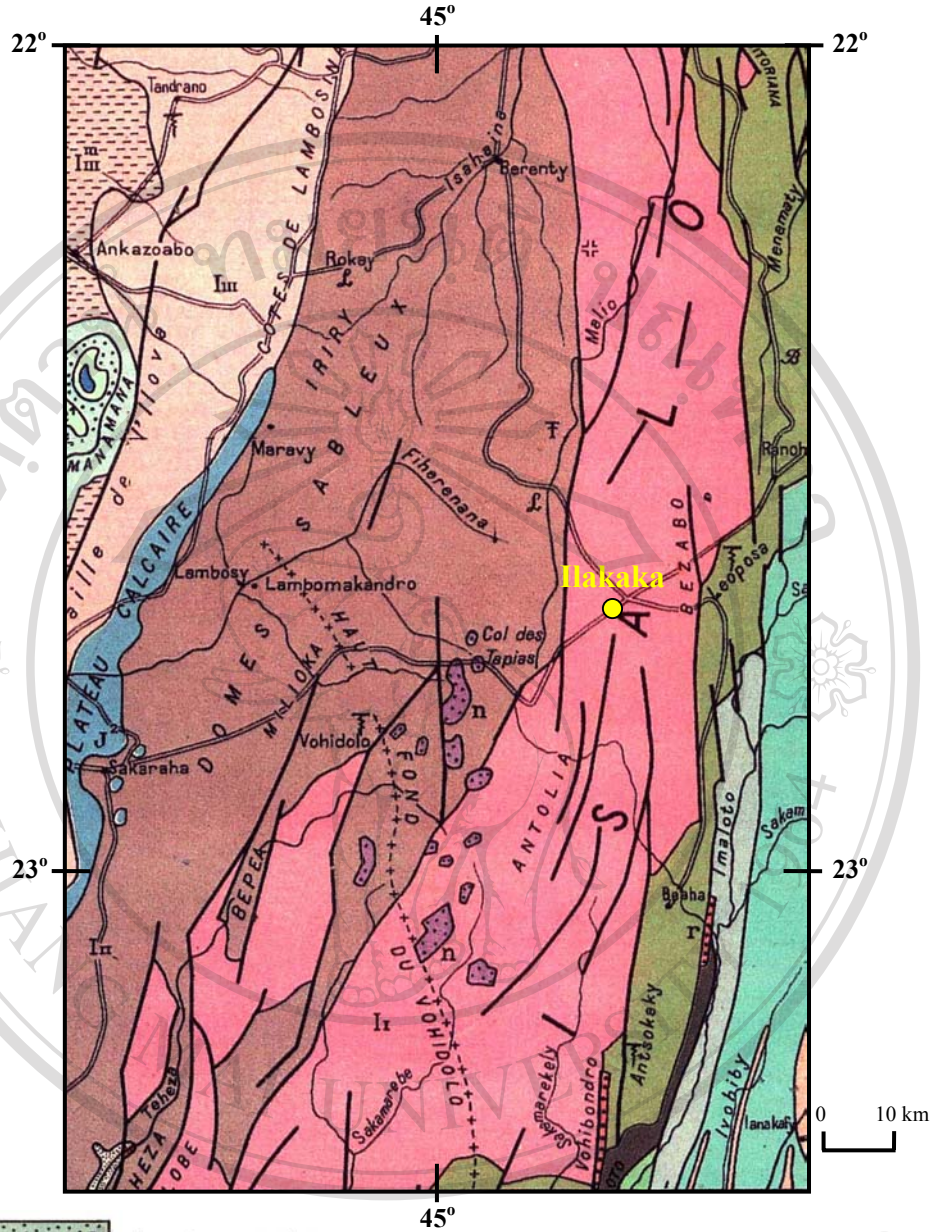


Figure 1.2 Geologic map of south-west Madagascar (Modified from Besairie, 1964).



Figure 1.2 Simplified geographical map of south-western Madagascar (Milisenda and others, 2001).

More than 70% of sapphire found there are fancy colour (pink, violet, orange, orangy pink, purplish pink, pinkish purple, brownish red, yellow and green). The natural blue colour stones are around 15%. The others are colourless sapphire and geuda. The associated minerals in this area consist of beryl (aquamarine and emerald), chrysoberyl (alexandrite and cat's eye), garnet (colour-changed garnet, hessonite and rhodolite), quartz (amethyst, citrine, colourless quartz and smoky quartz), spinel, spodumene (kunzite), topaz (blue, colourless, pale blue and pale yellow), tourmaline (dark yellow-green to red-brown, brownish pink and pink), zircon (brown, green and yellow) (Hänni, 1999; Schmetzer, 1999; Laurs, 2000; Chikayama and Furuya, 2001; Henn and Milisenda, 2001; Milisenda and others, 2001; Gem Mining Resources Corporation, 2002).

1.2 Causes of Colour

Corundum is an oxide mineral in which oxygen is combined with one or more metal. It consists of a ratio of two atoms of aluminum and three atoms of oxygen that is structurally classified in hematite group (Themelis, 1992; Hughes, 1997). The structures of the hematite group are based on hexagonal closest packing of oxygens with the cations (Al) in octahedral coordination between them (Figure 1.3). A basal projection of corundum shows that only two-thirds of the octahedral spaces are actually occupied by Al^{3+} cations (Klein and Hurlbut, 1999).

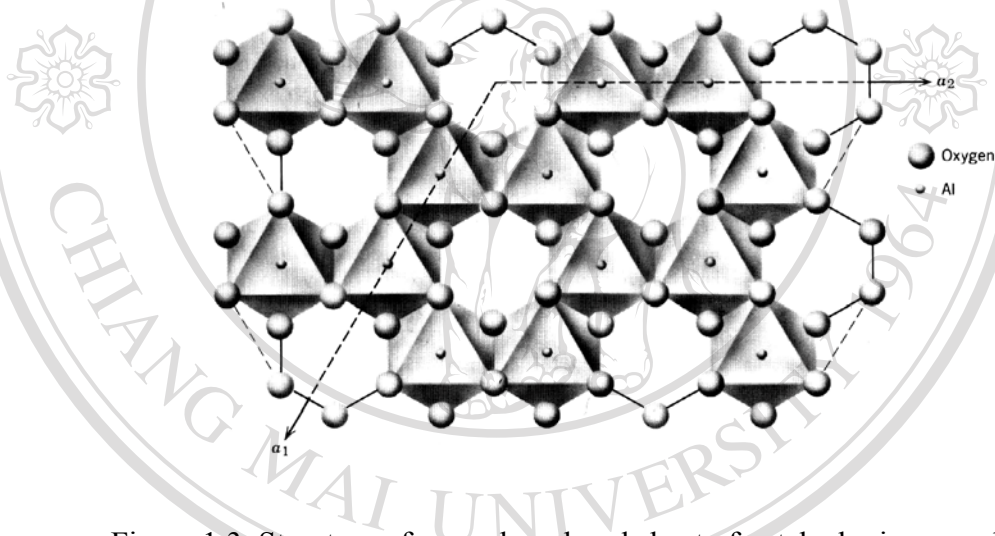


Figure 1.3 Structure of corundum, basal sheet of octahedra in corundum, with one octahedron vacant for every two octahedra with Al in centre (Klein and Hurlbut, 1999).

In the purest form, corundum is colourless. The colours of corundum are due to trace elements, which are transition metal elements, that can absorb some energy range of visible light. These elements may be present in corundum as impurities, replacing some aluminum atoms in the crystal lattice (Themelis, 1992; Emmett and others, 2003). Table 1.1 shows causes of colour in corundum.

Table 1.1 Causes of colour in corundum (Themelis, 1992; Hughes, 1997).

Colour	Transition metal impurities
Red, Pink	Cr ³⁺
Blue	Fe ²⁺ /Ti ⁴⁺
Yellow	Fe ³⁺
Orange	Cr ³⁺ and Fe ³⁺
Green	Fe ²⁺ /Ti ⁴⁺ and Fe ³⁺
Purple, Violet	Cr ³⁺ and Fe ²⁺ /Ti ⁴⁺

1.3.1 Ruby and Pink Sapphire

The colour of ruby and pink sapphire is due to trivalent chromium (Cr³⁺), which substitutes trivalent aluminium (Al³⁺) (Nassau, 1983; Fritsch and Rossman, 1987; Themelis, 1992; Hughes, 1997). The electronic arrangement of chromium atom can be designated as 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹. When electrons are lost, chromium becomes Cr³⁺. Cr³⁺ can substitute Al³⁺ in corundum because their ionic radii are closely similar. When white light passes through ruby, two absorption mechanisms occur. One, 2.2 eV light can be absorbed to take the chromium from the ⁴A₂ ground level to the ⁴T₂ excited level. This energy corresponds to absorption in the yellow-green part of the spectrum. The other mechanism, 3.0 eV light takes it to the ⁴T₁ level, and absorbs in the violet part of the spectrum (Nassau, 1983) (Figure 1.4).

About 0.1% of Cr³⁺ in corundum produces red colour. The intensity of colour is related to the concentration of the Cr³⁺. As the concentration of the Cr³⁺ is reduced, the red colour is reduced accordingly; thus, about 0.04% of Cr³⁺ will produce intense pink, whereas about 0.03% of Cr³⁺ will produce light pink (Themelis, 1992).

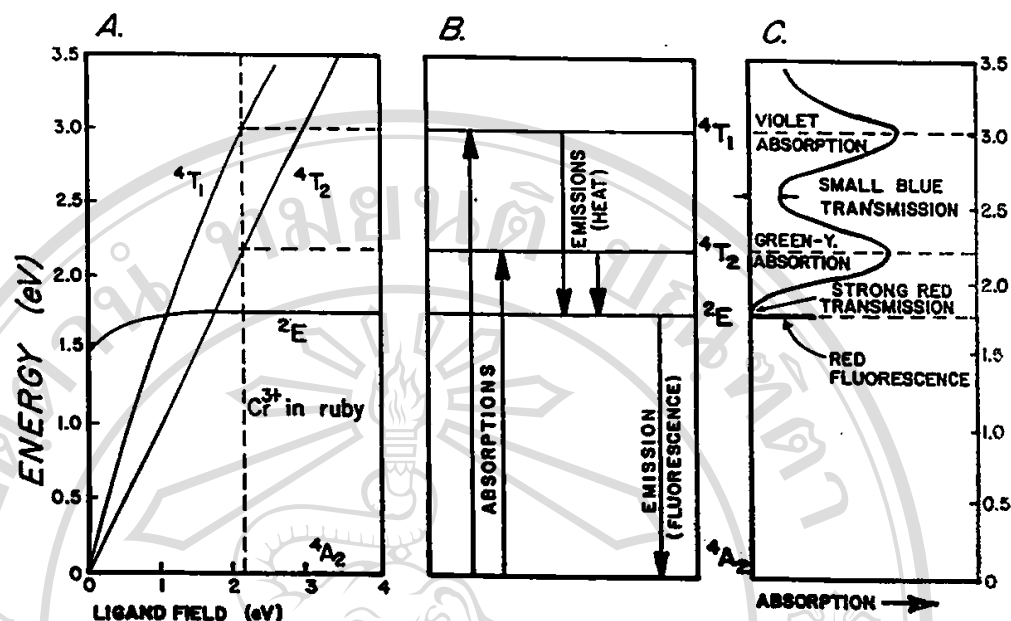


Figure 1.4 The term of Cr³⁺ in a distorted octahedral ligand field (A), the energy level and transitions in ruby (B), and the resulting absorption spectrum and fluorescence of ruby (C) (Nassau, 1983).

1.3.2 Blue Sapphire

The blue colour in corundum is mostly due to Fe²⁺-O-Ti⁴⁺ intervalence charge transfer (IVCT) process (Nassau, 1983; Fritsch and Rossman, 1988; Themelis, 1992; Hughes, 1997). This process is sometimes also called “cooperative charge transfer” (Nassau, 1983). If sapphire contained only a small amount of Fe²⁺, or only Ti⁴⁺, it would remain colourless. However, when both Fe²⁺ and Ti⁴⁺ are present at the same time and are on neighboring lattice sites, the blue is produced (Emmett and Douthit, 1993). The range between Fe³⁺ and Ti⁴⁺ ions is 2.65 Å⁰ (Figure 1.5), and there is enough overlap between d orbitals of these ions that it is possible for an electron to pass from Fe²⁺ ion to Ti⁴⁺ ion as follows : (Nassau, 1983)



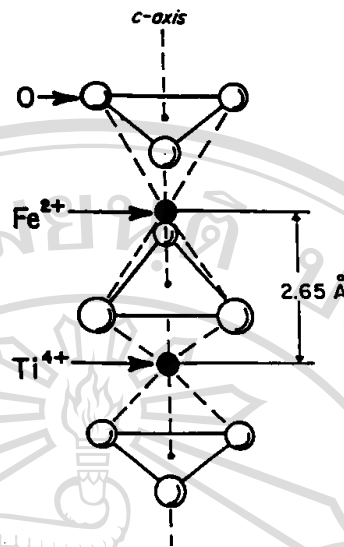


Figure 1.5 Two adjacent octahedral sites containing Fe^{2+} and Ti^{4+} in blue sapphire (Nassau, 1983).

The energy of this new combination of the right-hand side of equation is higher than that of the left-hand side by 2.11 eV. If the light of this energy falls on blue sapphire, it is absorbed while producing the charge transfer of equation. The result light of all colours but blue and violet-blue will be absorbed. In ruby requires 0.1% of chromium oxide to produce deep red, but blue sapphire requires only one-tenth of one percent, of both iron and titanium oxides (Nassau, 1983).

Besides, $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfer process can also produce the blue colour (Fritsch and Rossman, 1988; Themelis, 1992; Fritsch, 1993; Hughes, 1997). Fe^{2+} and Fe^{3+} ions can substitute in the lattice of corundum crystal to produce enough levels that eventually would be converted into colour (Themelis, 1992). The blue colour generated by this mechanism appears to be significantly grayer than the colour produced by $\text{Fe}^{2+} - \text{O} - \text{Ti}^{4+}$ charge transfer, such as corundum from Australia, China, Thailand and Cambodia (Fritsch, 1993).

1.3.3 Yellow Sapphire

Yellow is due to $\text{Fe}^{3+}/\text{Fe}^{3+}$ pairs (Fritsch and Rossman, 1988; Themelis, 1992; Emmett and Douthit, 1993; Hughes, 1997). The Fe^{3+} can substitute the Al^{3+} of corundum as iron oxide, Fe_2O_3 . Two Fe^{3+} ions are close enough to produce electron transition (Themelis, 1992; Emmett and Douthit, 1993). The other cause of yellow sapphire is hole colour centres, one electron missing from an atom.

The area of colour centres is resulted from substitution of Mg^{2+} in the lattice (Fritsch and Rossman, 1988; Themelis, 1992; Emmett and Douthit, 1993; Hughes, 1997). Thus, one electron is added in the lattice. When corundum is heat treated under highly oxidizing conditions, a hole is created in the lattice which has an effective electrical charge of +1. This hole combines with the Mg^{2+} , providing the +3 charge required at that lattice site (Emmett and Douthit, 1993). Besides, the colour of yellow sapphire can be the result of combination of Fe^{3+} and colour centres (Themelis, 1992).

1.3.4 Green Sapphire

The combination of blue and yellow produces green. The colour of green sapphire is produced by combination of $\text{Fe}^{2+} - \text{O} - \text{Ti}^{4+}$ IVCT and $\text{Fe}^{3+}/\text{Fe}^{3+}$ pairs. Various ratios of $\text{Fe}^{2+} - \text{O} - \text{Ti}^{4+}$ IVCT and $\text{Fe}^{3+}/\text{Fe}^{3+}$ pairs produce green, bluish green, yellowish green and similarly appearing colours (Themelis, 1992; Emmett and Douthit, 1993; Hughes, 1997).

1.3.5 Violet / Purple Sapphire

Similarly, the colour of purple/violet sapphire is due to a combination of red and blue colours. Fe^{2+} and Cr^{3+} , often with $\text{Fe}^{2+} - \text{O} - \text{Ti}^{4+}$, produce dark violet sapphire, whereas purple sapphire is caused by Cr^{3+} and $\text{Fe}^{2+} - \text{O} - \text{Ti}^{4+}$ IVCT (Themelis, 1992; Emmett and Douthit, 1993; Hughes, 1997).

1.3.6 Orange Sapphire

The orange colour is due to a combination of red and yellow colours. In orange sapphire, the colour is a result of varying amounts of Cr^{3+} often combined with varying amounts of Fe^{3+} (Themelis, 1992). Also, colour centres which are due to Mg or Mg and Fe can produce orange colour when the Mg-content exceeds the Fe+Ti-content (Häger, 2001).

1.3.7 Padparadscha

Padparadscha, a Singhalese word, means lotus flower and refers to orangy pink or pinkish orange sapphire. This colour is due to Cr^{3+} and colour centres, often modified by Fe^{3+} . Cr^{3+} is also present, adding a pink tint and thus producing a pinkish orange colour (Themelis, 1992; Hughes, 1997). Some orange sapphires from the Uмба River Valley (Tanzania) and Malawi are often termed padparadscha. These sapphires contain Cr^{3+} as orange and pink colour components; the yellow component is due to Fe^{3+} . No colour centres are present (Themelis, 1992).

1.3 Heat Treatment

Gemstone enhancement has been going on for hundreds of years. Many techniques have been used to improve the appearance of gems. Treatments involve heating, diffusion, irradiation, fracture/cavity filling, coating, impregnation, dyeing, bleaching, and laser drilling. In corundum, treatments typically involve heating, diffusion, cavity filling and dyeing (Kammerling and others, 1990; Smith and McClur, 2002; Aber, 2003). Heat treatment is accepted more than the other treatments because the process improves something which is in natural gemstones so that they look better.

The factors which are used to determine the quality and value of gemstones are referred to the 4Cs. These factors are colour, clarity, cutting and carat. Colour is the most important determinant of value in gemstones. The good colour is considered from the even distribution and the intensity of the colour. Clarity is based on what can be seen when gemstones are examined using 10x magnification. The clarity grade is important because it indicates how clean the gemstones are, the cleaner stone is the more valuable. Cutting can affect the beauty, durability and cost of the gemstones. The cutting of gemstones is important because of its effect on the depth of colour, the liveliness, the fire and brilliance exhibited by the stone. Carat is a unit of weight. The greater the weight, the greater the value per carat (Matlins and Bonanno, 1993).

Heat treatment is a process which can change the colour and the clarity of the stone. Colour can be developed, intensified or lightened. Clarity can be improved by removing various impurities that produce haziness (Themelis, 1992; Emmett and Douthit, 1993; Hansawek, 2001; Smith and McClure, 2002).

One of the earliest references to gem treatments is found in Pliny's History of the world, written by C. Plinius Secudus (born 23 AD and died 79 AD). He discussed many gemstone enhancement techniques which have been used until today; almost 2000 years later, including foils, oiling, dyeing and composite stones (Hughes, 1997; Nassau, 1999).

About 1240 AD, the Arabic writer Teifaschi described in detail the heat treatment methods used by the Arab gem merchants to improve the colour of ruby in Sri Lanka (Themelis, 1992; Hughes, 1997). Similarly, Duarte Barbosa also discussed the heat treatment of Sri Lanka rubies (Hughes, 1997).

In 1635, John Baptista Porta, in the sixth of his Natural Magic, mentioned a detailed account of "how to turn a sapphire into diamond" through the process of heating. In another segment of the same work, he described, "how to make a stone

white on one side and red or blue on the other,” by plastering one side with chalk and subsequent heat treatment (Themelis, 1992; Hughes, 1997).

The nineteenth century is an era which produced many gemmological text books about heat treatment of corundum, such as : (Themelis, 1992; Nassau, 1999)

- *A Treatise on Diamonds and Precious Stones* of Mawe in 1813, reports that, “intense heat cannot change the ruby.”,
- *A Treatise of Gems* of Feuchtwangler in 1838, reports that, “if the red sapphire (ruby) is exposed to a great heat, it becomes green, but when cold, returns to its original color.”,
- Kluge in 1860, mentions the loss of colour in sapphire and the removal of spots and other defects in ruby,
- *Precious Stones and Gems* of Streeter in 1892, reports that, “rubies are occasionally infected with white spots which can be removed by burning.”,
- and *Edelsteinkunde* of Bauer in 1896, describes the effects of intense heat treatment on Burmese ruby and sapphire.

The heat treatment of ruby and sapphire was performed regularly in Europe by the turn of the twentieth century. In 1932, Wild provides some detailed information that heat treatment produces certain changes within the molecular structure of the minerals, and reports that gems which are changed by heat are blue Ceylon sapphires, which change to faint yellow-white at 400 °C and purple Ceylon sapphires, which change to pink at 450 °C. In 1947, Ulrich Guhler published *Studies of Precious Stones in Siam*. He reported that the ruby does not lose its colour when heated (Themelis, 1992).

In Thailand, the heat treatment of zircon has been well-known for 100 years. Most of the rough stones are from Bo Kha, Cambodia. Later, the heat treatment of corundum was accidentally discovered in 1959 by Mr. Sammuang Kaewwaen during sapphire-jewelry fabrication (Themelis, 1992; Hansawek, 2001). Those corundums are natural milky blue sapphires called geuda. Geuda, a Sinhalese word, describes a certain grade of low quality sapphire which is found mainly in Sri Lanka (Hughes,

1997). Intense heat, applied to a gold ornament adjacent to light-blue sapphire, resulted in the stone's turning darker blue (Themelis, 1992). Then, the heat treatment process has been developed until today.

Perera and others (1991) heated around 50 stones of the "ottu" variety all with dark blue patches on the outer surface in the temperature range 1,800 to 1,850 °C for one hour under reducing conditions. The results were classified into three types. They were :

- | | |
|--------|--|
| Type A | Clear blue stones : good blue colour and clarity. |
| Type B | Clear stones that did not attain a satisfactory colour : insufficient blue colour but good clarity. |
| Type C | Stones with a non-transparent white coating : formation of a thick white precipitate ("dead milk") on the outer surface. |

When the initially heated stones were re-heated in the temperature range 1,600 to 1,800 °C under oxidizing conditions, types A and B showed a reduction of blue colour. No change was observed in type C stones.

Pemadasa and Danapala (1994) heated Sri Lankan corundums which can be classified into two groups, according to the temperature and oxidation-reduction conditions used for heat treatment. Under oxidizing conditions, they heated bluish rubies at 1,000 °C for one hour to remove blue colour. Ruby and pink sapphire, that display geuda characteristics, were heated at 1,500 °C for two hours. Kowangu yellow sapphires (slightly yellowish) were heated at 1,800 °C for half an hour.

The other groups of corundum consist of two principal varieties, geuda and ottu, each of them can be further subdivided into four and two subvarieties, respectively. They are heated in reducing conditions at various temperatures and soaking time to develop blue colour. The temperature of heating ranges from 1,750 to 1,900 °C , and the soaking time ranges from 10 minutes to one hour. Table 1.2 shows the subvarieties, the temperatures and the soaking times of geuda and ottu sapphires.

Table 1.2 The subvarieties, the temperatures and the soaking times of geuda and ottu sapphires (after Pemadasa and Danapala, 1994).

Variety	Subvariety	Temperature	Soaking time
Geuda	Silky geuda	1,900 °C	1 hour
	Milky geuda	1,850 °C	30 minutes
	Waxy geuda	1,859 °C	1 hour
	Dun geuda	1,750 °C	10 minutes
Ottu	Ethul ottu	1,750 °C	20 minutes
	Pita ottu	1,750 °C	20 minutes

In 1997, Themelis (cited in Johnson and Koivula, 1997) heated pink geuda sapphires from Vietnam. Most of the stones were opaque and cloudy, with pronounced milkiness. He performed three heat-treatment experiments on rough stones. First, pink geuda sapphires were heated at 1,650 °C for five minutes in air, followed by rapid cooling (30 °C/minute). Most of them turned blue, ranging from light to very dark, and developed patches or zones of blue. The others turned pink or purple. In a second experiment, he heated pink geuda sapphires that had a more noticeable pink tinge and obvious milkiness, at 1,675 °C for 10 minutes in pure oxygen and followed by rapid cooling. Most of them turned medium-to-intense pink, and the others turned medium blue. Last, pink geuda sapphires were heated at 1,700 °C for 10 minutes under reducing conditions and followed by rapid cooling. They turned very dark blue almost black, purplish blue to blue and mottled blue, with concentrated patches of blue colour all over their surface (Johnson and Koivula, 1997).

Siripaisarnpipat and others (2000) heated Mong Hsu rubies, which had blue core, at various temperatures (900 1,400 1,500 1,550 1,600 1,650 and 1,700 °C), with heating rate of 329 °C/hour and soaking time of two hours. Besides, they varied the heating rate (260, 331, 433 and 650 °C/hour) at 1,600 °C and two-hours soaking time. At the heating rate of 260 °C/hour, and the temperature of 1,600 °C, they varied

the soaking time (0.5, 1, 3 and 4 hours). The result was that the higher temperature ($>1,600\text{ }^{\circ}\text{C}$) and longer soaking time can reduce the blue core better than the lower temperature and shorter soaking time. The heating rate did not influence the blue core.

1.4 Aim and Objectives

The main aim of this study is to determine the heat treatment process for sapphires from Ilakaka, Madagascar, with electric, oil and gas furnaces at various conditions.

The objectives of this study are :

1. To determine the appropriate heat treatment configuration for Ilakaka sapphires.
2. To explain the change after heat treatment using scientific concepts.