INFLUENCE OF HEAT TREATMENT ON BERYLS FROM BARARATA AND ANALAKELY-VOHAMBOHITRA ANKAZOBE QUARRIES, MADAGASCAR : COLOR IMPROVEMENT AND GEMMOLOGICAL IMPLICATIONS

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ABSTRACT

This study examines the impact of heat treatment on beryls extracted from the Bararata and Analakely-Vohambohitra-Ankazobe quarries in the Analamanga region of Madagascar. The samples, initially yellow and green in color, were heated to 400°C to intensify their blue hue. The results show that the reduction of Fe^{3+} to Fe^{2+} in the beryl crystal structure significantly enhances the saturation of blue tones, particularly in aquamarines. However, treatment temperatures that are too high, as observed at 450°C, can lead to complete discoloration of some gems. Strict control of heat treatment parameters is therefore essential to maximize the value of gems while avoiding their degradation. The study also highlights the economic importance of the region's pegmatites, which are rich in beryl and other precious minerals such as quartz and tourmaline.

Keywords : *Beryl, heat treatment, Vohambohitra-Ankazobe, Madagascar, aquamarine, gemmology, pegmatite*

INTRODUCTION

Beryl is a precious gemstone with several varieties, valued for its unique colors, which are primarily influenced by chromophores such as iron, chromium, and vanadium. In Madagascar, the Vohambohitra-Ankazobe region in Analamanga is geologically rich in LCT (Lithium-Cesium-Tantalum) granitic pegmatites, known for being significant sources of gem-quality beryls. The Bararata and Analakely quarries, situated in this region, are renowned for producing beryls in various colors, including blue, green, and yellow. These beryls are often heat-treated to intensify their blue hues, a process widely accepted in the gemmological industry. This treatment, particularly for aquamarines, modifies the oxidation states of iron in the crystalline structure, enhancing both their visual appeal and market value. The mineral wealth of this region solidifies its status as a key location for gem extraction and research in Madagascar.

1. GENERAL

Beryl ($Be_3Al_2(Si_6O_{18})$) is a cyclosilicate mineral composed of six silica tetrahedra arranged in rings, forming a highly stable hexagonal structure. Beryllium and aluminum atoms occupy the cavities formed by these tetrahedral rings. With a hardness of 7.5 to 8 on the Mohs scale and notable chemical resistance, beryl is a highly valued gemstone. It exists in several varieties, the most famous of which include aquamarine (blue-green), emerald (green), and heliodore (yellow). The color variations in beryl are attributed to the presence of chromophoric elements, primarily iron, chromium, and vanadium, which substitute for certain elements within the crystal structure (Hughes, 1997).

Light blue to blue-green varieties, such as aquamarine, derive their color from the presence of Fe^{2+} within the crystal structure, while heliodore, ranging from yellow to golden, owes its color to Fe^{3+}. Green beryl, excluding emerald, typically results from the coexistence of both Fe^{2+} and Fe^{3+} (Nassau, 1984). In contrast, emerald's vivid green color is primarily due to the presence of chromium (Cr^{3+}), and sometimes vanadium (V^{3+}), which replace aluminum in the crystal structure (Giuliani et al., 2000).

The Vohambohitra-Ankazobe region in the Analamanga province of Madagascar is a geological domain abundant in pegmatites, which serve as the primary sources of gem-quality beryl. This region lies within the Antananarivo Neoarchean domain, dating back approximately 2500 Ma, and is characterized by magmatic intrusions such as the Ambalavao-Kiangara-Maevarano suites. These suites consist of stratified granites, as well as gneissic and migmatitic host rocks (Razafiarisoa, 2015). The geological formations in this area are home to pegmatites, renowned for their wealth of minerals, including beryl, tourmaline, coltan, and various types of quartz (Roig, 2007). The pegmatites here are classified as LCT (Lithium-Cesium-Tantalum) pegmatites, often associated with rare and valuable minerals like gem-quality beryl (Cerny, 2005)

The Bararata and Analakely quarries (Fig. 1), situated near the Vohambohitra massif, are key sites for beryl extraction. These quarries are notably rich in yellow, blue, and green beryl (Fig. 3). The pegmatite veins in this region are typically zoned, with minerals deposited in successive layers around a central core, a characteristic feature of granitic pegmatites (Černý, 2005). Additionally, these veins are accompanied by other industrial minerals, such as smoky quartz, mica, and black tourmaline (schörl). The mineral inclusions present in the region's quartz and beryls reflect complex crystallization conditions, often occurring at low temperatures, which favor the formation of large minerals (Razafiarisoa, 2015).

In gemmology, aquamarine and heliodore are highly valued for their clarity and color. Aquamarine, in particular, is prized in the jewelry industry for its intense blue hue. High-quality stones are frequently heat-treated to remove greenish tints and enhance their blue color, a practice widely accepted in the gemmological industry, as long as it is disclosed (Schmetzer, 1984). Heat treatment at approximately 400°C can transform the color of green or yellow beryls into a more vibrant blue by altering the oxidation states of iron within the crystal structure (Wood and Nassau, 1968). This process is especially applied to aquamarines from Madagascar, where pegmatites are known for yielding high-quality gems (Loeffler and Burns, 1976).

In this region, the interplay of ancient tectonic activity and specific crystallization conditions has resulted in the formation of exceptionally high-quality beryls, further enhancing the economic significance of these deposits. The unique geological conditions at Vohambohitra, coupled with the mineral richness of the pegmatites, make this area a key focus for both gemologists and geologists, serving as a crucial site for scientific research and industrial exploitation

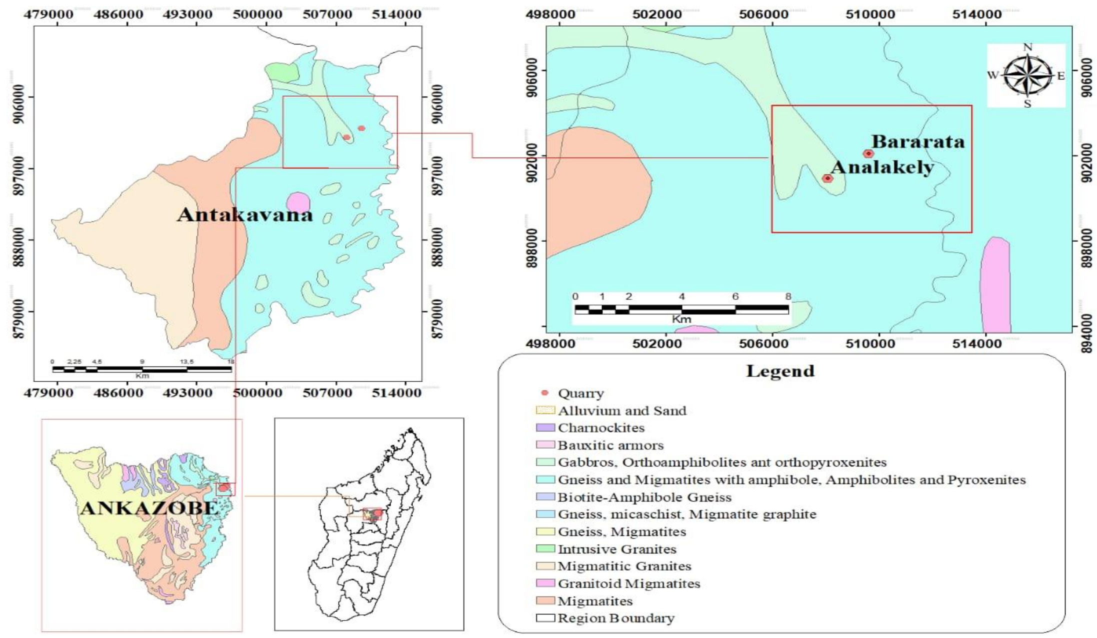

Fig-1 Geological map and geographical location of the beryl deposits of Analakely and Bararata (modified by RAZAFIMAROSON, 2024)

Fig-2 (A) Analakely quarry and (B) Bararata quarry (RAZAFIMAROSON, 2024)

Fig-3 (A) Some raw aquamarine samples from the Analakely quarry (B) Yellow-green beryl on quartz matrix from the Bararata quarry (RAZAFIMAROSON, 2024)

2. METHODOLOGY

2.1 Preliminary work

Geographical and geological data from the Bararata and Analakely quarries were analyzed, with field observations conducted to collect beryl samples. Prospecting was guided by local geomorphology and outcrop mapping.

2.2 Laboratory work

All laboratory work was conducted at the Gemmology Laboratory, Faculty of Sciences, University of Antananarivo. Classical gemmological analyses were performed on 51 beryl samples, categorized by color as blue (26 samples), green (17 samples), and yellow (8 samples). These analyses involved the use of a 10X magnifying glass, refractometer, spectroscope, and polariscope to identify the optical and internal properties of the gems prior to heat treatment.

Before heat treatment, the samples were meticulously prepared. First, they were cleaned with 90° alcohol to remove any surface impurities. The samples were then sorted by size to ensure uniform heat distribution. Each sample was carefully wrapped in specialized aluminum foil made of alumina (Al_2O_3), with a melting point of 2072°C and a thickness of 0.02 mm. This protective coating prevented direct exposure to high temperatures, minimizing the risk of degradation.

Heat treatment was performed using a Mestra TS 80 series electric furnace, which can reach a maximum temperature of 1200°C, with an adjustable heating rate ranging from 0 to 20°C per minute. The heating cylinder was prepared by filling it with fine sand, primarily composed of quartz, to help maintain and stabilize the internal temperature during the heating process. The samples were then arranged in layers within the cylinder, based on their size, to ensure even heat distribution throughout the treatment..

The heating procedure began with a gradual increase in temperature to 450°C, achieved over the course of 1 hour and 20 minutes. The purpose of this gradual temperature rise was to gently heat the samples, minimizing the risk of cracking or structural alteration. Once the target temperature was reached, it was maintained for 45 minutes to ensure the samples achieved complete thermal homogeneity.

The cooling process was carefully controlled to prevent thermal shock. First, the oven was switched off, and the samples were left inside the cylinder for 35 minutes. Afterward, the cylinder was removed from the oven and allowed to cool outside for an additional 20 minutes.

The materials used in this experiment included 50 cm tongs with a rounded head for handling the cylinder, the Mestra TS 80 series electric furnace for heating the samples, fine sand to regulate the internal temperature, and aluminum foil to protect the samples during treatment. After heat treatment, the beryl samples were carefully observed to assess color changes and verify that their internal structure remained intact. The heat treatment notably enhanced the color of the beryls, particularly the yellow and green varieties, which transformed into a more intense blue, thereby increasing their gemological value

2.3 Workshop work

The raw beryls were cut using lapidary techniques and subsequently used to craft jewelry. The gemstones were set in silver and white gold settings to evaluate their potential for jewelry applications.

3. RESULTS AND INTERPRETATION

The gemological properties of the beryl samples studied show refractive indices ranging from 1.570 to 1.598 for the ordinary ray (n_o) and from 1.565 to 1.590 for the extraordinary ray (n_e), varying based on the specimens' colors and varieties. These values align with those recorded in other gem-bearing regions (Smith, 2001). The birefringence, ranging from 0.005 to 0.008, reflects the minor differences between the refractive indices, characteristic of beryl's hexagonal crystal system (Johnson et al., 2010). Density measurements, performed using a precision balance, reveal values between 2.66 and 2.80 g/cm³, consistent with the standard physical properties of different chromatic beryl varieties (Jones, 2005). In terms of transparency, the samples range from transparent to translucent, depending on internal inclusions (Doe, 2012).

Sample A001 exhibited a greenish-yellow hue before heat treatment, attributed to the presence of Fe^{3+} in its crystalline structure. After heat treatment at 400°C, the sample developed a light blue hue, explained by the reduction of Fe^{3+} to Fe^{2+} (Nassau, 1984). This color change diminished the yellow and greenish tones in favor of a purer blue, thereby enhancing the visual quality of the sample. Sample B002, which initially showed a yellowish-green hue also due to the presence of Fe^{3+}, took on a more intense blue hue after heating to 400°C, driven by the same reduction of Fe^{3+} to Fe^{2+}, further intensifying the blue saturation and increasing the sample's value (Wood and Nassau, 1968). In contrast, Sample A004 displayed a yellow hue before treatment, indicative of a higher Fe^{3+} concentration. Following treatment at 450°C, the sample became colorless, likely due to excessive heat treatment that removed most of the chromophores, leading to complete discoloration (Loeffler and Burns, 1976). These observations demonstrate that heat treatment can effectively transform less valuable beryls into more desirable gemstones, but it is crucial to carefully control the treatment conditions to prevent adverse effects such as discoloration.

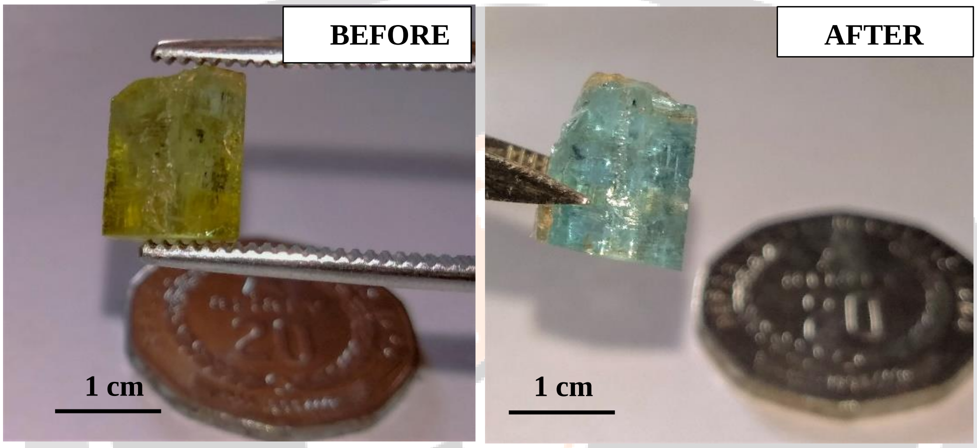

Fig-4 *Sample* A001 had a greenish-yellow hue before treatment, and after heating to 400°C, it took on a ligh blue hue.

Fig-5 Sample B002 had a yellowish-green hue before treatment, and after heating to 400°C it took on a blue hue

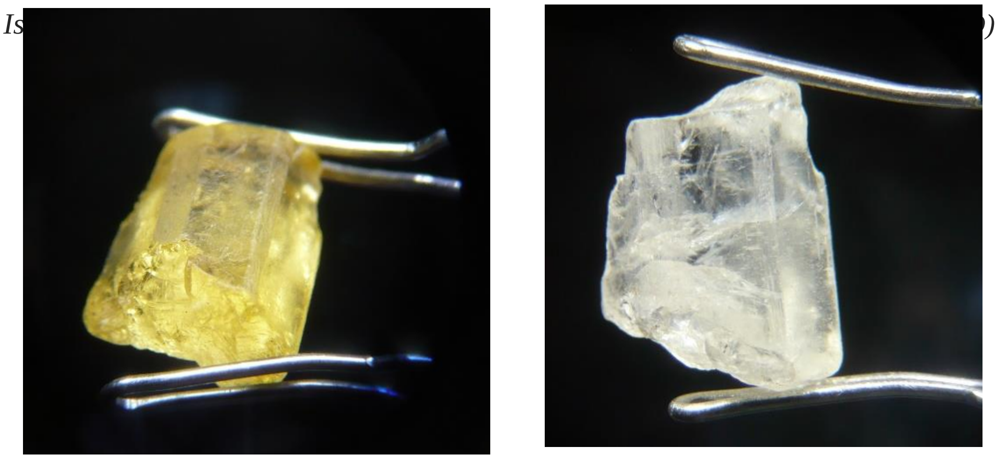

Fig-6 Sample A004, initially yellow, became colourless after heat treatment at 450°C.

4. DISCUSSION

The results obtained in this study confirm the significant impact of heat treatment on beryls by altering their initial hues. The heating process enhanced the color of the samples, depending on their chemical composition, particularly the presence of Fe^{2+} and Fe^{3+}, which are critical in the coloration of beryl varieties (Nassau, 1984). The findings indicate that yellow and green samples developed more intense blue hues following heat treatment, especially in aquamarines, where the blue color is attributed to the presence of Fe^{2+}. In contrast, heliodores containing Fe^{3+} experienced the disappearance of their yellow tones (Wood and Nassau, 1968).

The transition from green or yellowish hues to light blue shades in certain beryls, as observed in samples A001 and B002, is attributed to the reduction of Fe^{3+} to Fe^{2+} within the crystal structure under the influence of heat. This process enhanced the saturation of the blue color, aligning with the gemmological market's expectations for high-quality aquamarines (Schmetzer, 1984). These findings are consistent with previous research, which indicates that heating beryls to around 400°C is optimal for intensifying blue hues by eliminating unwanted greenish tones (Loeffler and Burns, 1976).

However, the results also underscored the risks associated with excessively high processing temperatures. Sample A004, after being heated to 450°C, lost all its color and became colorless, a consequence of the decomposition of the chromophores, leading to discoloration (Loeffler and Burns, 1976). This outcome highlights the critical importance of precisely controlling heat treatment conditions to avoid degrading the quality of the gemstone.

The Vohambohitra-Ankazobe region has proven to be a key site for the extraction of high-quality beryls, with heat treatment significantly enhancing the commercial value of the gems sourced from this area. Additionally, the variety of minerals found in the region's pegmatites, including quartz, tourmaline, and coltan, further strengthens the economic potential of these quarries, not only for gemmology but also for other industries that exploit these resources (Razafiarisoa, 2015; Roig, 2007).

Although heat treatment is an effective method for enhancing beryls, careful control of temperature and time parameters is crucial to achieve optimal results without compromising the integrity of the gemstones.

CONCLUSION

This study demonstrated the effectiveness of heat treatment in improving the colour of beryls extracted from the Vohambohitra-Ankazobe quarries in Madagascar, particularly for aquamarine varieties. The reduction of Fe^{3+} to Fe^{2+} under the effect of heat has made it possible to transform yellow and green hues into more intense shades of blue, thereby increasing the value of the gems on the market. However, it was observed that excessive heat treatment, at 450°C, could lead to total discolouration of the samples, underlining the need for precise control of heating conditions. In addition to the value of the gems, this region of Madagascar has great economic potential thanks to the wealth of rare and precious minerals in its pegmatites. The results of this study therefore highlight the importance of heat treatment in optimising the quality of beryls and pave the way for future research into heat treatment parameters to maximise their gemmological potential.

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