The Origins and Analyses of Gem Corundums

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By

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FOREWORD

Colorful and pretty stones, what we now call gemstones or gems for short, have attracted humans since they first walked this Earth. This is simply due to their beauty. Those that are rare and valuable are called precious gemstones. Gemstones are found in many places on Earth and areas where they are particularly concentrated are called gem fields. The gem varieties of corundum (Al_2O_3) are known as sapphire (generally blue, green, and yellow) and ruby (generally pink to red) and these are particularly concentrated in South East Asia and Australia where they have been mined for centuries.

This book on sapphires and rubies by my colleague, Dr. Seriwat Saminpanya, is dedicated to the history, properties, chemistry, structure, and formation of these precious gems. It is an essential book on these gems and should be of great interest to anyone fascinated by them. I now invite you to delve deeper into the wonder of sapphires and rubies.

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PREFACE

The author has been kindly invited by Cambridge Scholar Publishing (CSP), with the invitation extended by Helen Edwards, the former Commissioning Editor, allowing the author to write the book “The Origins and Analyses of Gem Corundum”. The author is in debt to Alison Duffy, the current Commissioning Editor, and the staff of the CSP who have been very patient in getting this book published. The author has dedicated a significant amount of time to composing the contents of this book, which are expected to captivate a diverse audience including gemologists, mineralogists, geologists, university students in related fields, and the general public. Ruby and sapphire, two well-known varieties of gem corundum, hold immense appeal for many individuals due to their beauty, high value, and exceptional durability. This book meticulously examines the characteristics of rubies and sapphires, explores the mineralogical significance of corundum, presents advanced techniques for their study, and delves into the origins and occurrences of these gemstones, which encompassed the geological processes of corundum formation and the specific localities, often referred to as the countries of origin. Other important information includes the synthetic processes and old/new treatments on corundum, which will be very beneficial for readers seeking to distinguish these stones from their natural counterparts. In this regard, the author has been working with corundums since his M.Sc. and has continued his research in the area through his Ph.D., as well as in his teaching and research work at the university. The book would not be complete without the contributions of several individuals, including Dr. Ian T. Graham from the Earth and Sustainability Sciences Research Centre at the School of Biological, Earth and Environmental Sciences, University of New South Wales Sydney (UNSW Sydney), Australia. Dr. Graham dedicated significant time to scrutinizing, proofreading, and providing invaluable feedback on the manuscript. Special thanks are also extended to Dr. Frederick Lin Sutherland, a senior Fellow of the Geoscience & Archeology, Mineralogy and Petrology section at the Australian Museum Research Institute, for his meticulous review of the manuscript. The photos and images have been contributed by various individuals and publishers, and their names appear in the photo and figure captions. The author hopes that the contents of this book will prove very helpful to the readers, supporting their work and fulfilling their passion. Finally, gratitude is extended to Cambridge Scholar Publishing for providing this excellent opportunity to share knowledge about corundum with people worldwide.

INTRODUCTION

The origins of gem corundum have long been an enigma, and hopefully, this book will shed new light on the origins of this gemstone from various global locations. Recently, research related to gem corundum has attracted significant worldwide interest. Although their synthetic counterparts are readily available, the gem market has recently changed due to consumer demand for natural stones of known geographic origin. This book will illustrate the varieties and origin of natural corundum and associated minerals. Conditions of corundum formation will be discussed. Trace element fingerprinting, stable isotopes, and mineral inclusions are key features for explaining the origin and sources of gem corundum. The story can be linked to the corundum's rock types and geological occurrences. An extensive review has been made of high-impact factor peer-reviewed journal articles and books, as well as research projects conducted by the author. The book will be beneficial to individuals of all interests and learning levels, including mineralogists and geologists researching the origins of gem corundum, university students, gem traders, gemologists working in laboratories, lapidaries, and the general public. The book will also act as a reference guide for traders, aiding them in determining the likely geographic origin of their stones. This is due to the limited availability of printed books of this type on the market. The book offers insights into the genesis of gem corundum and presents advanced techniques for corundum analysis worldwide.

Research on corundum has increased in the past few decades, but the knowledge gained from it is mainly published in scientific journals. With the growing database of corundum from worldwide deposits, this book contributes to our ever-growing understanding of the geological evolution of this mineral. The book will take a leading role in explaining the science of gem corundum research in such a way that it will be easy to digest and read by a variety of audiences.

Seriwat Saminpanya, PhD

CHAPTER 1

WHAT IS GEM CORUNDUM?

Although emery (corundite) and dark opaque granular corundum grains have long been used as abrasives, they have been obscured by colored stones such as ruby and red spinel. During the last few decades, the gem corundums mined from Madagascar are unparalleled (Kiefert *et al.*, 1996; Schmetzer, 1999), with half of the current world's supply coming from this country. Rubies are mined from Andilamena and Vatomandry while sapphires are mostly exploited from Ilakaka and Sakara (Dill, 2010). Other countries are also important in producing rubies and sapphires for the world market while possessing valuable unique geological occurrences to be studied. This chapter presents the background of corundum. In the beginning, the root names and certain folklore of this mineral are discussed. These will be followed by physical, optical, and chemical properties; gem corundum varieties; and corundum structure.

1.1 The root names of corundum and history of usage

The word "corundum" originated from the Tamil language, "kuruntam" which means ruby. The word "corundum" is from "kurunvinda" which means "hard stone" in the Sanskrit language, and may be from the word "kurmidam" in the Tamil language. The word was changed to "kurund" in the German and Dravidian languages (Anthony *et al.*, 1990; Giuliani *et al.*, 2014). The word "ruby" originated from "ruber" in the Latin language and the word "ratnaraj" in the Sanskrit language. The words mean the queen of valuable gemstones and the emblem of fire. The root of the word "sapphire" is not exactly known. It may be from the word "sauriratna" in the Sanskrit language and changed to "sappheiros" in the Greek language and then "sapphirus" in the Roman language (Giuliani *et al.*, 2014).

In the 18th century, there was a major contribution by French scientists who mineralogically characterized "corundum" as a distinct mineral species for the first time. In 1784, ruby and sapphire were testified by Romé de l'Isle as corundum species. In 1787, the specific gravity (SG) of corundum was first reported by Brisson. In 1802, Chenevix first established the chemical compositions of corundum. From 1894 to 1921, Lacroix and his team conducted field studies in Madagascar. In 1922, they published a three-volume book on Madagascan mineralogy, focusing on corundum. This is the first book on the world's corundum deposits. A corundum of blue color is generally named "sapphire". The corundums of other hues except red (ruby) are collectively called "fancy sapphire". In gemology, a color term affixed by the word sapphire is more straightforward or makes more sense, for example, blue sapphire, yellow sapphire, green sapphire, etc. The other valuable variety with a pink-orange or orange-pink color and moderate to low saturation is called padparadscha after the color of the lotus flower (Crowningshield, 1983; Giuliani *et al.*, 2014). The term "ruby" is used for corundum which exhibits a red color. Other colors, such as orange-red, blood-red (pigeon blood red), purple-red, brown-red, or pink-red may be accepted for ruby.

The next part will focus on the mineralogical properties of corundum, in terms of group, species, and varieties. The crystallography of different varieties will be discussed. The mineral chemistry of corundum as a variation in chemical composition vs. physical and optical properties is the main focus of this chapter.

1.2 Structure of corundum

Corundum is a crystalline material, occurring in nature as a mineral or of artificial origin as its synthetic counterpart. The aluminium and oxygen atoms arrange themselves to make this material stable in a regular pattern called networks or structures. The structure of corundum or aluminium oxide (α-Al_2O_3) is approximately one of hexagonal close packing of oxygen (**Fig. 1-1, a**), with the polyhedral representation of octahedral coordination of O^{2-} ions surrounding the Al^{3+} ions. Pairs of octahedra share faces (face-sharing octahedra) or two neighboring AlO_6–octahedra share a common face forming "groups" of 2Al and 9O atoms. Two-thirds of the octahedrally coordinated interstices are filled with Al-cations. The O-ions are coordinated by distorted tetrahedra of four Al-cations (Beran, 1991; O′Keeffe and Hyde, 1996: 222). **Fig. 1-1, b)** shows a portion of the corundum lattice. Oxygen ions are found on the equally spaced planes but aluminium ions are between the planes. Aluminium ions occur at sites about one-third or two-thirds of the distance between two planes of oxygen ions. Certain distances in the structure are given in angstrom, Å (Geschwind and Remeika, 1961). The Al–O distances are 3x1.97 Å and 3x1.86 Å (Newnham and De Haan, 1962). In **Fig. 1-1,** distorted octahedral oxygens around an Al ion are shown in two different ways compared to the regular octahedron

(Nassau, 1983). The Cr^{3+} ion (center) is surrounded by six neighboring oxygen ions in ruby. Three oxygen ions in the upper layer rotated ca 4.3° from a regular position, viewed along the trigonal crystal axis (optic axis) (Shinada *et al.*, 1966 in Henderson and Imbusch, 1989: 421). The structure diagrams for corundum in different crystal directions can be found in Giuliani *et al.* (2020).

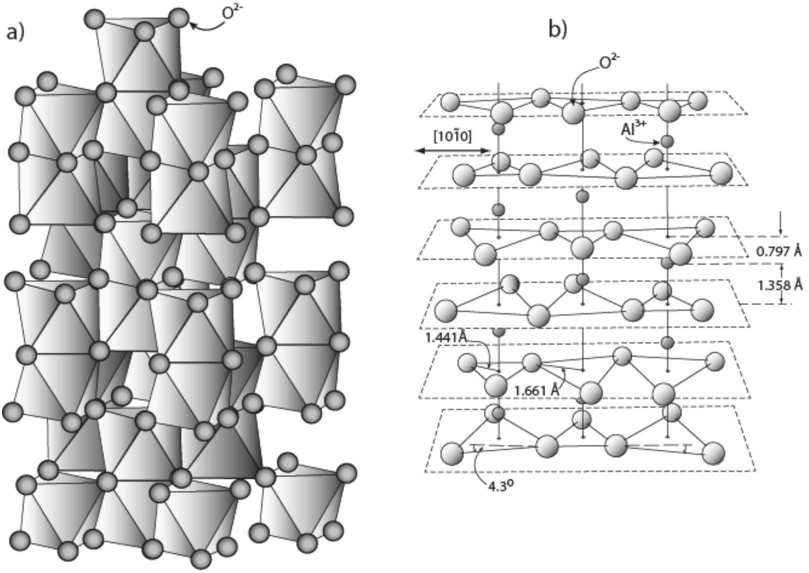

Fig. 1-1 The structure of corundum, **a)** after O′Keeffe and Hyde, 1996, Crystal structures, I. Patterns and symmetry, Mineralogical Society of America Monograph. Washington, D.C.: Mineralogical Society of America, 453 pp., reprinted with permission from Dover Publications Inc., **b)** after Geschwind, S., Remeika, J.P., 1961. Paramagnetic resonance of Gd^{3+} in Al_2O_3. Physical Review 122, 757–761, (reprinted with permission from American Physical Society).

The corundum structure is organized as a compact rhombohedron or hexagon. A vertical *c*-axis has a length of 12.96 Å and each of the horizontal *a*-axes has a length of 4.75 Å. This makes a high ratio of *c/a*, 2.73 (Kronberg, 1957; Heuer *et al.*, 1998; Dobrovinskaya *et al.*, 2009).

There are 17 slip systems of dislocation in the structure, with this, there are 8 slip planes (Snow and Heuer, 1973). Under higher temperature conditions, the *c*-slip (basal-slip) system is prominent (Kronberg, 1957; Snow and Heuer, 1973; Lagerlöf *et al.*, 1994; Nakamura *et al.*, 2002).

Oxygen ions in the structure of corundum are arranged nearly hexagonal close-packing (HCP) and two-thirds of octahedral sites are occupied by Al ions. The space group of corundum was investigated by Pauling and Hendricks (1925) and it has been designated as R3–c, meaning that there are 6 formula units in a hexagonal unit cell (Pajączkowska *et al*., 2001).

1.3 Physical, optical, and chemical properties of corundum

Corundum, with the chemical formula of Al_2O_3 or aluminium oxide, is the name of the mineral species under the hematite (Fe_2O_3) mineral group, based on their identical crystal structure. Corundum is in the mineral oxide class. As a simple oxide, a metal (Al) links with oxygen (Klein, 2002). In its structure, an aluminium atom is linked with six oxygen atoms (O), indicating that the aluminium has a coordination number of six (CN = 6), or that aluminium is in the octahedral site. The Al is in the middle of six surrounding oxygen atoms. Corundum has several dominant physical properties. It possesses a high hardness (resistance to abrasion) of 9 on the Mohs scale. It is the 3rd hardest material after diamond (hardness = 10) and moissanite (hardness = 9.25). As the Mohs scale is relative, corundum is actually four times softer than diamond. The great hardness comes from its strong covalent bonding between Al and O in its structure, giving rise to a high luster up to bright vitreous on its well-polished surface. However, depending on its surface condition, sometimes a subvitreous or dull luster can occur.

Both the strong covalent bonding and how the molecules are arranged in the structure of corundum lead to a high melting point (2050°C). With the well-packed structure, corundum has a high density or specific gravity of 3.90 to 4.05. Note that the density and the specific gravity values for a particular material are the same, however, density has the unit of gram/cubic centimeter, but there is no unit for specific gravity as it is a relative measurement (weight in air versus weight in water). With its high SG, then its refractive index (RI, represents the ratio of the speed of light in air to its speed in the material) is also high (1.758 to 1.780). Based on crystallographic systems, corundum crystallizes in the trigonal system (UK) or rhombohedral division (US). This system has a structure possessing four reference or crystallographic axes (imaginary axes running through the crystal by passing through the atom or reference points in the structure and all axes must have an origin at the center of the crystal). Three horizontal axes (*a1, a2*, and *a3*) are of the same length and are 60 degrees apart from the first axis to the next axis. The last one is a vertical axis (*c*) which is perpendicular to these three horizontal axes.

Because the crystallographic structure controls the passage of light through crystalline materials, as a result, corundum has two different RIs or two different rays, so-called ordinary ray RI (n_ω or ω) and extraordinary ray RI (n_ε or ε). This is because when light travels through the corundum crystal it splits into two different rays or ray paths (o-ray or ω-ray and e-ray or ε-ray). Therefore, any direction with this property is called an anisotropic direction. Materials that behave in this way are collectively called anisotropic materials. Corundum has an optical characteristic or optic sign that is negative (–), due to $n_\varepsilon < n_\omega$. The difference between the lowest RI (n_ε) and highest RI (n_ω) (birefringence) of corundum is about 0.009. It is important to realize that any crystalline material with $n_\varepsilon > n_\omega$ will have a positive (+) optic sign. Each of these two rays is plane-polarized, with the light rays propagating perpendicular to each other. These light rays travel at different velocities, causing corundum to have two different RI values. This phenomenon is related to the vibration of light and sometimes corundum acts as a polarizing filter. Corundum is also classified as a double refraction (DR) mineral based on its optical characteristics. Due to the corundum structure, light can travel through it in any direction, causing the light to split into two orthogonal polarization directions in most cases. However, there is a unique direction along the vertical reference axis (*c*-axis) where the light ideally remains unpolarized or does not split. In this direction, the velocity of light remains constant, characterized by a refractive index denoted as ω. This direction is known as the optic axis, where the light exhibits isotropic behavior. Corundum, possessing only one isotropic direction, is classed as a uniaxial mineral, meaning it has only one optic axis. Some minerals have two optic axes; they are classed as biaxial minerals. Biaxial materials include crystalline materials and minerals crystallized in orthorhombic, monoclinic, and triclinic systems. Some materials interact with light waves in the same way in all directions, without causing the light waves to split. These materials are called optically isotropic or isotropic materials. They include materials crystallized in the cubic (isometric) system and amorphous substances. These materials are classified as single refraction (SR) materials and have a single refractive index (RI) value.

Corundum interacts with ultraviolet radiation and gives a luminescent appearance. Many minerals do not fluoresce due to lacking energy levels to allow for ultraviolet absorption or visible light emission. There are activator elements such as Cr and V causing fluorescence in corundum, whereas Fe is the extinguisher for fluorescence in the stone or it can prevent or reduce the emission of fluorescence in ruby and sapphire. An exception, an unusual light bluish sapphire can fluoresce very faint pink-orange under long-wave ultraviolet (LWUV). This sapphire contains Cr, Fe, and Mg, and insignificant concentrations of Ga and Ti. This sapphire also shows a color change effect (light blue under incandescent light and blue-violet under fluorescent light or daylight) (Gaievskyi *et al.*, 2014). Many varieties of corundum naturally fluoresce under visible white light, such as rubies from Mogok, Myanmar. This fluorescence aids gemologists in identifying stones originating from this location, often resulting in significantly higher values for these gemstones. Natural and synthetic stones have certain different degrees of fluorescence. For example, the Verneuil flame fusion synthetic ruby always shows strong red fluorescence under the LWUV compared to its natural counterparts. Rubies from Myanmar are brighter red fluorescent under ultraviolet than Thai rubies which are richer in the Fe extinguisher to the fluorescence. Robbins (1994) summarized the fluorescent characteristics of varieties of corundum, which is a very useful guide for both gemologists and mineralogists. The fluorescence in ruby can also be detected as two narrow bands located in the red area of the white light spectrum. Some heated sapphires may react with ultraviolet radiation differently from unheated stones (*e.g.*, Hughes, 2018a). However, this technique is a supportive test and other confirmation identifications should be used. The fluorescent effect can help determine the geographic origin of some sapphires. For example, orange fluorescence in blue sapphire indicates a Sri Lankan origin (McClure *et al.*, 2019).

Pure corundum has a molecular weight of 101.96 with a relatively high density (3.98 g/cm^3) and a high refractive index. Natural corundum, α-Al_2O_3, is alumina that is renowned for its high hardness, wear resistance, electrical insulation, thermal shock resistance, less sensitivity to chemical reactions, and high tensile strength (Rouquerol *et al.*, 1999; Ye *et al.*, 2017). Corundum possesses a specific heat of 105 J/(kg·K) at 91 K (Kelvin) and 761 J/(kg·K) at 291 K. At 323 K, it possesses a thermal expansion coefficient of about 5.5×10^{-6} per Kelvin along its *c*-axis and about 7.7×10^{-6} per Kelvin at right angles to its *c*-axis. Corundum does not dissolve in water, HF, H_2SO_4, HCl, HNO_3, or H_3PO_4 under conditions of <300°C, and also in alkali solutions at <800°C (Ye *et al.*, 2017).

Some corundum may have a magnetic susceptibility or the stone attaches to a strong magnet due to the higher contents of Fe and Ti which are in the form of inclusions, *e.g.*, stones from the Republic of Liberia, (Williams and Williams, 2016). Aggarwal and Ramdas (2019) have covered almost all physical and optical properties of corundum in their monograph. They include crystal structure and growth, physical properties (compressive strength, hardness, Young's modulus, tensile strength, thermal expansion, thermal conductivity, and specific heat), optical properties (transmission, refractive index, absorption, Brillouin scattering, Raman scattering, and Cr-doped/Ti-doped lasers). The information and constant values in the monograph are useful for material scientists, mineralogists, and gemologists.

1.4 Gem varieties of corundum

The terms gem, gemstone, or gem material belong to any material which possesses beauty, rarity, durability, or value. Some gems lack durability such as amber and pearl but their beauty can be fascinating to many people. Corundum is more desirable than many other colored stones as it has a high ranking of its properties, *e.g.*, beauty (luster and color), durability (hardness, toughness, and stability), etc. Most corundum in the world is value-added to be used as a gem material in the markets by cutting, polishing, and/or treatment. A smaller market share of corundum is for industrial uses when it is not of gem quality. Such stones contain abundant inclusions, and fractures, and have low transparency. The synthetic counterparts are mostly for industrial uses. Some low-quality stones are enhanced to gem quality grade by heating to improve their color and to fill any fractures or cavities etc. Gem corundums are almost exclusively in high demand in the markets and there are several varieties based on their colors, inclusions, and phenomena apparent in the stone. As a general rule, except for the red stones, people call all corundum of other colors (blue, green, yellow, orange, pink, violet, and colorless) as “sapphire”. A more accurate name can be used by placing the color of the stone as a prefix to the word “sapphire” (*e.g.*, “colorless sapphire”, “pink sapphire”, “blue sapphire”, “violet sapphire”, “yellow sapphire”, “orange sapphire”, and “green sapphire”) (**Fig. 1-2**).

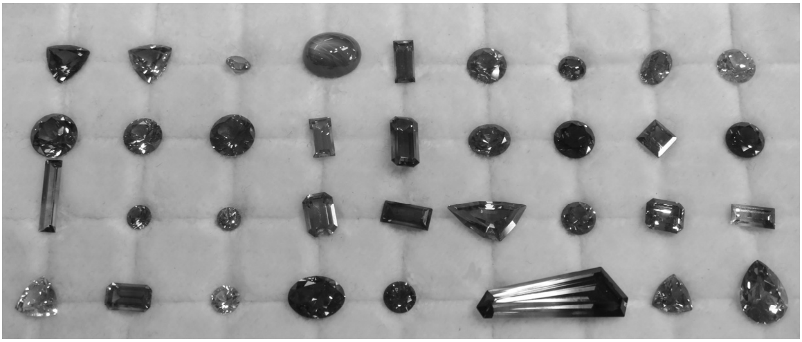

Fig. 1-2 Gem corundums in different colors and different carat weights from the Anakie Gem Field, Australia (Image courtesy of Dr. Ian T. Graham; largest stone is approximately 10 mm in maximum length). *See centrefold for this image in colour.*

The following are examples of the varieties of corundum:

1) Ruby: corundum with colors including red, orange-red, red-orange, blood-red (also known as pigeon blood red), purple-red, pink-red, or brown-red. If the ruby has a star effect, then it is simply called a star ruby. Trapiche ruby contains inclusions forming a star/flower-shaped pattern. The trapiche ruby is rarely found but such stones have been exploited from the Mong Hsu deposit in Myanmar, Nepal, Pakistan, Tajikistan, and Vietnam (see Schmetzer *et al.*, 1996; Sunagawa, 2003; Sunagawa, 2005; Liu, 2015; Giuliani *et al.*, 2020). The ruby of the pigeon blood color (vivid red color) is the most sought-after. It should be noted that the term “ruby” used in this book will include the above-mentioned and other colors, *e.g.*, pink, and pinkish-purple as well.

2) Blue sapphire: the stone has a blue color or any shade of blue. If blue sapphire has a star effect, then it is simply called star blue sapphire. Certain sub-varieties of blue sapphire are also known (*e.g.*, imperial blue sapphire, cornflower blue sapphire). Trapiche sapphire is a sapphire in which inclusions form a star-shaped pattern. Most people perceive that only blue-colored corundum is called “sapphire” but this is not officially used in a gemology context.

3) Purple sapphire: the stone has a purple color or different shades of purple.

4) Padparadscha: the stone has a pink-orange color, similar to that of a pink lotus.

5) Leuco sapphire: corundum appears to have a white or off-white color and is translucent.

6) Golden sheen sapphire or “Gold Sheen” or “Zawadi” (gift from the Earth) sapphire is a sapphire displaying an attractive metallic sheen or golden (bronze) color. The body color of this stone can be yellow, blue, or green. The sheen is attributable to light reflecting from needle or platelet inclusions of Fe-Ti oxide minerals *e.g.*, rutile, hematite, and ilmenite. The needles crystallized concordant with the trigonal structure of their corundum host can give a 6-ray or 12-ray star (asterism) effect seen in cabochon cut samples. This kind of sapphire was mined from eastern Kenya, near the border with Somalia (Bui *et al.*, 2015; Bui, 2019).

7) Colorless sapphire: corundum has no color hue and is transparent.

8) Parti-colored sapphires (parti sapphires or polychrome sapphires): corundum with two or three colors in a single stone, such as in blue, green, and/or yellow colors as well as the rare stone of blue, purple, or lavender colors.

9) Fancy sapphires: gem-quality corundum with any colors other than the above-mentioned. These include yellow sapphires, green sapphires, and orange sapphires.

Note that sometimes it can be very difficult to express the color of the stone. For example, a pink sapphire may be defined as a pale purple sapphire by different observers. A pale red-orange ruby may be judged as an orange sapphire. Geochemical classification can be helpful to designate the variety such as ruby has to be Cr-rich. Color determination is very subjective when dealing with other colored stones, *e.g.*, there is no clear boundary between ruby and pink sapphires (Krzemnicki *et al.*, 2020). Care must be taken when considering a particular color of corundum.

1.5 Summary

Corundum is a mineral species under the hematite mineral group which is in the oxide class. It has a chemical composition or formula of Al_2O_3. The word "corundum" is derived from the Tamil language, "kuruntam" meaning "ruby". In Sanskrit, "kurunvinda" means "hard stone". Corundum is also from "kurund" in German. The word "ruby" originated from the Latin term "ruber" and the Sanskrit term "ratnaraj". The word "sapphire" was derived from "sauriratna" (Sanskrit), "sappheiros" (Greek tongue), and "sapphirus" (Roman term). Corundum has a structure approximating one of the hexagonal closest packing of oxygens with an Al^{3+} ion surrounded by octahedral coordination of 6 O^{2-} ions. Face-sharing octahedra or two neighboring AlO_6–octahedra share a common face forming "groups" of 2Al and 9O atoms. It has a compact hexagonal or rhombohedral structure. Corundum has several dominant physical properties, *e.g.*, a high hardness (9 on the Mohs scale), a high SG (3.90 to 4.05), high refractive indices (1.758 to 1.780 with a birefringence of 0.009), and a high melting temperature of 2050°C. It crystallizes in the trigonal system (UK) or rhombohedral division (US) and its optical characteristics classify it as a uniaxial negative mineral. Cr and V cause fluorescence in corundum, especially Cr/V–bearing stones. Fe is an extinguisher for fluorescence in corundum. Gem corundum is divided into many varieties depending on the color and visual appearance, *e.g.*, red-colored stones are called ruby, stones of other colors, and stones possessing certain phenomena are named by affixing the term sapphire/ruby after the color, *e.g.*, blue sapphire, star ruby, and star sapphire. There are some special varietal names such as padparadscha, trapiche ruby, golden sheen stones, and parti-colored sapphires.

CHAPTER 2

MINERALOGICAL SIGNIFICANCE AND TREATMENTS OF CORUNDUM

In this chapter, various uses of corundum will be briefly reviewed. Specifically, the chapter discusses the significance of the mantle in the origin of some gem corundums, as well as the uses of corundum beyond gemstone purposes. Additionally, treatments that influence the chemical, physical, and optical properties of corundum, such as heat, bulk diffusion, glass filling, and high pressure and high temperature (HPHT) treatments, will be presented here.

2.1 The significance of the mantle in the formation of some gem corundums

Corundum is believed to be the first compound of major elements condensed from a hot solar gas (MacPherson, 2003). On Earth, corundums of mantle origin are more accessible. Several scholars have explained how some rubies and sapphires have crystallized in the mantle. Giuliani *et al.* (2015b) reported that the homogenous oxygen isotopic signature (O-isotope signature) of rubies, with values spanning those of mantle silicates, suggests that these rubies were derived from mantle xenoliths (pieces of rock trapped in magma that are different from the surrounding rock), such as pyroxenite or garnet lherzolite, or from metamorphosed gabbro or garnet clinopyroxenite xenoliths embedded in kimberlites at the lower crust. Pink sapphire samples from Mbuji-Mayi indicate a mantle source. They came from different parent rocks either from eclogite that was derived from the metamorphism of subducted oceanic crustal rocks or clinopyroxenite in the mantle. Chinese sapphire samples from Changle have a mantle O-isotope signature of syenitic magmas partially melted from a spinel lherzolite (Giuliani *et al.*, 2015b). Alkali basalt fields in Southeast Asia commonly contain mantle- and/or crustal-derived crystals of corundum, garnet, pyroxene, zircon, olivine, and plagioclase together with mantle xenoliths (garnet lherzolites, spinel lherzolites, and harzburgites) (Hoang and Han, 1990). The 380 Ma (million annum) old veins of ruby-bearing ultramafic rocks from Russia (Rai-Iz in Polar Urals) are believed to have formed in a peridotite mantle wedge. The activity of slab-derived melts/fluids has been recorded in the veins that reflect a circulation of materials between the crust and mantle. This process produced dunite and harzburgite with ruby and other minerals (Cr-spinel, oligoclase, paragonite, and phlogopite). The ruby exists as porphyroblastic to fine grains, containing 2–7 wt% of Cr_2O_3 and 92–98 wt% of Al_2O_3 (Meng *et al*., 2018). Isotope data of Ar, He, and Ne gases in corundum and associated mantle xenoliths of basaltic fields in Changle, China gave distinct constraints for the development of the subcontinental mantle. The $^3He/^4He$ ratio in the corundum is 7.6–8.3 times that of the atmospheric value, indicating the contribution of fluids from the convective asthenosphere (He *et al*., 2011).

Diamond as a mantle mineral has been found in alkali basalts. For example, diamonds occur within the eastern Australian intraplate basalt fields (Barrows *et al*., 1996). Additionally, rare diamonds can be found as an inclusion in corundum. For instance, Wilcock and Bosshart (1997) investigated a diamond accompanied with graphite inclusions in a sapphire sample from Ban Huai Sai, Laos. Diamonds accompanied by graphite and lonsdaleite inclusions in rubies, as well as graphite inclusions in sapphires, have also been described from Vietnam (Johnson and Koivula, 1997). However, corundum crystals have been found as inclusions in diamonds transported by kimberlite magmas (Hutchinson *et al*., 2004). In Brazil, the Juína kimberlite carried the diamonds containing inclusions of Cr-rich ruby, Al-rich pyroxene ($\leq$10 wt% Al_2O_3), Mg-perovskite, and Fe-periclase (Hutchinson *et al.*, 2001). The alluvial diamonds of Rio Aripuanã, Juína, Brazil contain ruby and sapphire inclusions. The inclusions exist as single grains and interlocking grains with Al-rich pyroxene and Fe-periclase. The mineral geochemistry and phase relationships suggest that diamonds of this nature originated at a mantle depth of approximately 770 km (Hutchison *et al*., 2004). A Cr-rich ruby (>8 wt% Cr_2O_3) has been found as a contemporary inclusion in a Type II diamond (without nitrogen) from the São Luiz alluvial deposit in Brazil, and its paragenesis is eclogite-grospydite (Watt *et al*., 1994). Moreover, corundum grains have also been discovered in other samples of eclogite-grospydite, a xenolith from the mantle (Dawson and Carswell, 1990; Watt *et al*., 1994). This indicates that corundum can endure a broad range of mantle circumstances (Gasparik, 1984; Harley and Carswell, 1990). The Cr-rich ruby from São Luiz reflects crystallization at a depth below the lithosphere (Watt *et al*., 1994). Corundum inclusions in zircon can also be found. For example, Sinh *et al*. (2019) discovered corundum and olivine inclusions in gem-zircon crystals from the alluvium of the basaltic field in the central highlands of Vietnam. The corundum crystals exhibit euhedral and subhedral forms without cracks and other inclusions, suggesting that they are primary inclusions that crystallized either before or simultaneously with their zircon host.

In the Democratic Republic of the Congo, ruby and sapphire crystals have been found as xenocrysts (foreign crystals that have been incorporated into magma from surrounding rock) (<1.5 cm across) in the kimberlite of Mbuyi-Mayi (Giuliani *et al.* 2015b). The colors of the ruby samples include red, red-violet, and pink, with a Cr_2O_3 of ≤5.6 wt%. The $\delta^{18}O$ data (5.55±0.05‰) suggests a mantle source (the mantle $\delta^{18}O$ value = 5.5±0.4‰; Mattey *et al.* 1994). In South Africa, at the Roberts Victor mine, xenoliths of kimberlite containing Cr-sapphire grains (<100 μm across) were found embedded in kyanite-eclogite xenoliths (Hatton, 1978). Additionally, Exley *et al.* (1983) and Mazzone and Haggerty (1989) reported the discovery of Cr-sapphire crystals in corganite and corgaspinite xenoliths at Jaggersfontein and Bellsbank mines. Furthermore, a ruby crystal rich in Cr (Cr_2O_3 ≤3.2 wt%), measuring approximately 150 μm in length, was found in a pyrope-spinel xenolith from the Moses Rock Dike in the state of Utah, USA (Padovani and Tracey, 1981). These findings collectively suggest the corundum can exist in the mantle or is a mantle-related mineral. However, the detailed information on the genesis of corundum in this category is scarce.

Zircon is commonly associated with corundum, either as inclusions within corundum crystals or found in alluvial deposits containing corundum. This association can provide valuable insights into the crystallization processes related to corundum in various contexts. Zircon can provide the ages of crystallization as it contains radioactive elements including thorium (Th), lead (Pb), and uranium (U). The decay process of parent and daughter isotopes, with a half-life resulting in 50% of remaining parent isotopes, allows for accurate dating of the zircon host (*e.g.*, Coenraads *et al.*, 1990; Sutherland *et al.*, 2002a; Abduriyim *et al.*, 2012; Link, 2015; Sutherland *et al.*, 2015a and 2015b; Akinin *et al.*, 2017; Filina *et al.*, 2019; Sutthirat *et al.*, 2020; Thi Anh Vu *et al.*, 2023). The problem is that some dated zircon megacrysts were collected from loose sediments or gem gravels in alluvial deposits, and one could argue that the results may not apply to associated corundums found in the same deposit. Therefore, great care must be taken when dating a zircon from an alluvial deposit, especially in interpreting the ages of associated minerals, as these may be transported from different source rocks. However, if syngenetic zircon inclusions in ruby or sapphire are dated, the results or ages are very reliable and make sense for the age of the co-existing corundum. The origin of zircon crystals associated with alkali basalt has been widely reported, nevertheless, it remains controversial (Hinton and Upton, 1991; Sutherland, 1996; Belousova *et al.*, 2002; Garnier *et al.*, 2005; Sutherland and Meffre, 2009). Some scientists believe that gem zircon and corundum crystals are xenocrysts carried by alkali basaltic magma and do not crystallize directly from the host magma (*e.g.*, Hinton and Upton, 1991; Saminpanya, 2000). Others believe that both zircon and corundum crystallized directly from alkali basaltic magma (*e.g.*, Griffin *et al.*, 2000; Hong-sen *et al.*, 2002; Visonà *et al.*, 2007; Baldwin *et al.*, 2017). Sinh *et al.* (2019) reviewed several hypotheses for the origin of zircon crystals in alkaline basalts and proposed three different origins for zircon in alkali basaltic areas as follows:

1) Crystallization from magma generated from a metasomatic reaction in the upper mantle, confirmed by O-isotope data (Sutherland, 1996; Upton *et al.*, 1999; Garnier *et al.*, 2005; Sutherland and Meffre, 2009).
2) Crystallization from an oceanic island basaltic magma with a process of late-stage fractionation (Belousova *et al.*, 2002; Griffin *et al.*, 2000).
3) Formation from a primeval alkaline mafic melt that subsequently developed to a lower alkaline composition (Visonà *et al.*, 2007).

The megacrysts of Cambodian zircon found in Cenozoic alkaline basalts formed through a metasomatic process involving Zr-rich silicate melts and/or phosphate-rich fluids (Cong *et al.*, 2016). Additionally, Piilonen *et al.* (2018) reported the discovery of zircon megacrysts as single grains embedded in alkali basalt at Ratanakiri suggesting that the megacrysts crystallized under carbonate-rich conditions.

Upton *et al.* (2009) studied felsic (salic) xenoliths of the "anorthoclasite suite", in alkali basalts from Scotland. These xenoliths mainly contain Ca-poor and Na-rich feldspar megacrysts, along with corundum, apatite, magnetite, zircon, biotite, and Fe-rich pyroxenes. The researchers suggested that the majority of the xenoliths were derived from the disintegration of Na-rich syenitic rocks. These syenitic rocks formed as sheets developed by the disintegration of felsic melt portions ascending from the shallow mantle before being incorporated into the basaltic magma. The anorthoclasite suite generally grows from metaluminous magmas (having a molar proportion of $Al_2O_3 < CaO+Na_2O+K_2O$). However, the occurrence of magmatic corundums in the xenoliths indicates that the corundums crystallized from peraluminous magmas (having a molar proportion of $Al_2O_3 > CaO+Na_2O+K_2O$).

Recently, Sinh *et al.* (2019) studied the zircon geochemistry and inclusions (corundum, olivine, and calcite) in zircon grains from a placer deposit in central Vietnam. They concluded that the zircon megacrysts were not directly crystallized from alkali basalt but had formed from carbonatite-influenced melt originating from the partially melted lithospheric mantle subjected to metasomatism. Note that carbonatite is a type of igneous rock formed from carbonatitic magmas in the deep mantle, primarily composed of carbonate minerals (*e.g.*, calcite and dolomite) with minor amounts of silicate minerals. The resorption and re-growth features were investigated using photoluminescence spectroscopy (PL), indicating an extended dwelling time in the magma chambers with variable rare-earth element (REE) contents at temperatures >900°C. The zircon xenocrysts were included in rising alkali basalts at about 6.5 Ma and 1.0 Ma (U-Pb ages). The direct finding of zircon megacrysts in the related basalts of Ratanakiri, Cambodia (Piilonen *et al.*, 2018) strongly supports this conclusion. Epigenetic inclusions in corundum (*e.g.*, baddeleyite, feldspar, hematite, quartz, and CO_2–H_2O fluids) indicate the basaltic melt and/or circulation of carbonate-bearing fluids in the later stage (Sinh *et al.*, 2019).

Palke *et al.* (2016) studied sapphire samples found in the dyke of ultrabasic lamprophyre at Yogo Gulch in Montana, USA. The samples showed corrosion features, suggesting that they were not in equilibrium with the lamprophyre that conveyed them to the Earth's surface. The silicate glass inclusions in the sapphires contained high Na and Ca contents and low Fe, Mg, and K contents, which differed from the composition of the lamprophyre host. The authors suggested that the sapphire crystallized from Al-rich protoliths that were partially melted from the lamprophyre at the lower crust. The sapphires crystallized at the peritectic point, where kyanite transformed to corundum, during kyanite melting. The mantle-derived melts likely reacted with the crustal rocks as they rose to the Earth's surface (Palke *et al.*, 2016).

Mantle-derived corundum, especially in an eclogite environment with high pressure and high temperature, such as that from India studied by Shimpo *et al.* (2006), provides a good example. The rocks, characterized by high Al and Mg contents, are found in the Palghat-Cauvery Shear Zone located in the Namakkal district (Sevitturangampatti), India. These rocks possess several mineral suites, including corundum + cordierite + garnet + Mg-staurolite + sapphirine + sillimanite + spinel, corundum + cordierite + garnet + Na-gedrite + sillimanite/kyanite, garnet + Mg-staurolite + sillimanite/kyanite, corundum + Mg-staurolite + Na-gedrite + sapphirine, corundum + biotite + sapphirine, and cordierite + Na-gedrite + sapphirine + spinel. Corundum and garnet exist as porphyroblastic coarse grains (0.1–10 cm across) within the sillimanite + cordierite + gedrite matrix. Kyanite is found as an inclusion within garnet. The presence of garnet+corundum, staurolite, and kyanite in the mineral suites of this locality suggests a high-pressure metamorphic condition characteristic of eclogite-facies with temperatures ranging from 940 to 990°C. This condition was a consequence of the Gondwana assembly during the late Pan-African Orogeny (Shimpo *et al.*, 2006).

Another example of xenoliths from the mantle related to corundum originates from a granulite environment, characterized by high-temperature and moderate-pressure metamorphism. This environment produces high-grade metamorphic rocks predominantly composed of feldspars and quartz. Alternatively, the xenoliths may originate from a metamorphic condition characterized by high temperatures and moderate pressures during tectonic mountain-building events, as shown by Sutthirat *et al.* (2018). They reported that xenoliths from both the deep crust and mantle are associated with Thai basaltic rocks in the Bo Rai area, where rubies are found. They classified the xenoliths into three main types:

1) Peridotites (composed of olivine, clinopyroxene, orthopyroxene, and spinel-bearing xenoliths),
2) Clinopyroxenites (composed of clinopyroxene, spinel, and garnet, with possible occurrences of olivine and orthopyroxene xenoliths), and
3) Mafic granulites (composed of clinopyroxene, plagioclase, and spinel, with possible occurrences of corundum and garnet).

These findings by Sutthirat *et al.* (2018) strongly support a mantle origin for certain gem corundums, emphasizing the significant role of the mantle in their formation. Type 3 xenoliths, which contain corundum, are particularly notable due to their metamorphic alteration as evidenced by mineral and whole-rock chemistry. Ruby samples from placer deposits associated with type 3 xenoliths formed at depths of 30 to 50 km, under pressures of 0.95 to 1.3 GPa and temperatures between ~700ºC and above 1000ºC. They were subsequently brought to the Earth's surface by basaltic melt. These mineral assemblages predate the Middle Triassic amalgamation of Sibumasu and Indochina, which initiated metamorphic processes within the xenoliths. Later, during the early Eocene, the contact between the Indian Plate and the Eurasian Plate likely induced further metamorphic changes. This geological activity, including transpression, expansion, and shearing events in Southeast Asia during the Cenozoic Era, contributed to the exhumation of corundum-bearing xenoliths to the Earth's surface, as documented by Sutthirat *et al.* (2018). If these events are indeed true, then the age of crystallization for corundum would be very old, possibly older