What is corundum and what are its basic qualities?

Module B. Precious Gemstones

Lesson 18: Corundum Mineralogy and Gemology

What is Corundum and What are its Basic Qualities?

Corundum is an aluminum oxide that commonly forms hexagonal barrel-shaped prisms that taper at both ends or as thin tabular hexagonal plates. It has a hardness of 9 on the Mohs scale, making it one of the most durable commercial gemstones, and no dominant cleavage. A high specific gravity of ~4.0 (most silicate minerals are ~2.6) results in corundum occurring in secondary placer deposits and recoverable by panning methods, similar to how you would recover placer gold. Refractive index of corundum is ~1.76 to 1.78.

Corundum comes in all colours of the rainbow but is most commonly found as opaque crystals with dull colours. Red corundum is called ruby, blue corundum is called sapphire, and all other colours are called fancy sapphires. Some varieties of corundum will fluoresce under short wave and long wave UV light if there is enough chromium in the crystal structure but little iron, which tends to quench any emitted energy.

What is its chemistry and crystal structure?

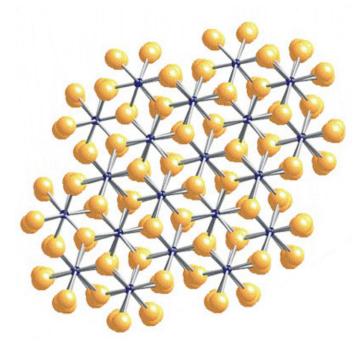
Module B. Precious Gemstones

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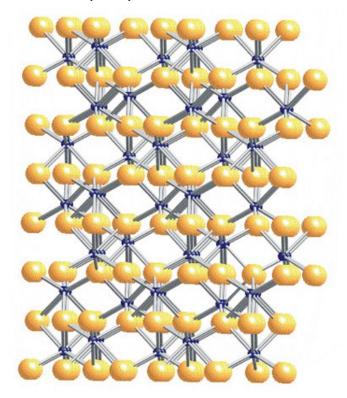
What is its Chemistry and Crystal Structure?

The base chemical formula for corundum is Al₂O₃. The aluminum (Al) in this simple formula is the key to generating the striking colours of corundum's gem varieties. Aluminum can be replaced by many of the transition elements, which are common chromophores (colour causing elements) in minerals.

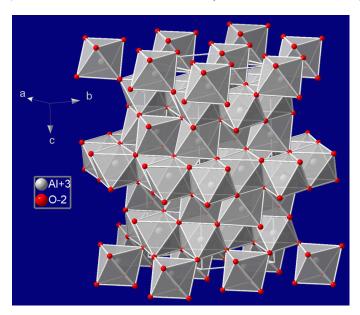
Each Al atom in the crystal bonds with six O atoms in the form of an octahedron. These Al octahedrons share some of their corners, edges, and faces with each other and consequently it is more intuitive to view the crystal structure of corundum using the ball and stick method instead of polyhedral method. However, the polyhedral model is still provided as the final image if you prefer to view the structure that way.



Ball and stick representation of corundum's crystal structure, looking down the *c*-axis.



Ball and stick representation of corundum's crystal structure, looking down the a-axis.



Polyhedral representation of corundum's crystal structure, looking between the a- and b-axis.

What colours can corundum have?

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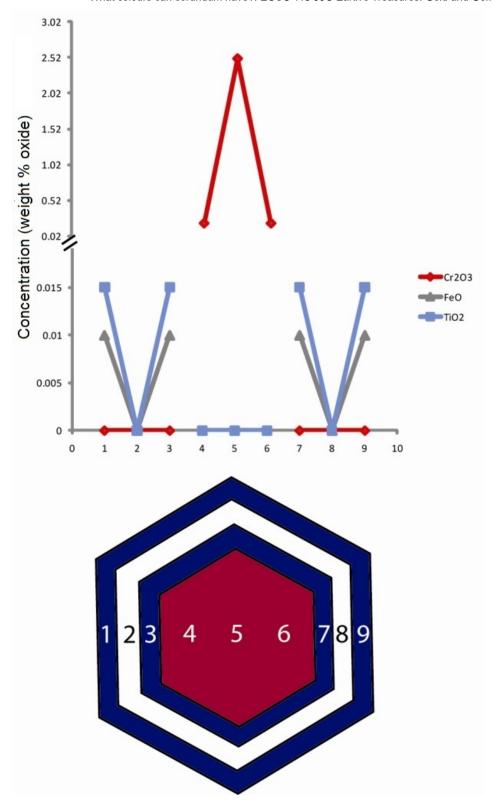
What Colours can Corundum Have, How are These Colours Generated, and What Gem Varieties Result?

Pure corundum is colourless and clear if transparent or pale white if opaque. This mineral also has low dispersion so the value of the stones comes not from fire generated (as in diamond), but rather from the intensity of colours seen. The vivid colours of corundum gem varieties, such as ruby and sapphire, arise primarily due to transition metal elements substituting for Al. The most common cations to substitute are Fe⁺², Fe⁺³, Ti⁺⁴, Cr⁺³, and V⁺³.

A continuum of colour saturation exists between pink sapphire and ruby that is correlated with trace amounts of Cr. There is no official cutoff for the amount of Cr needed for ruby, but usually rubies will have up to \sim 1 wt% of Cr_2O_3 . There is a trick up ruby's sleeve that makes its red almost jump out at the observer: When Cr is introduced into corundum it makes the mineral fluorescent under UV light. This means that UV energy from normal light is accepted into the crystal and then re-emitted at a lower energy level - conveniently in the red region, thus amplifying the intensity of red in ruby under daylight conditions. However, if any iron (Fe) is present it will usually absorb the red fluorescence from UV light. Thus, the finest rubies are those that have little to no Fe in their crystal structure.

Blue sapphires are generated primarily from pairs of Fe⁺² and Ti⁺⁴ substituting into the crystal structure for Al⁺³. The process of intervalence charge transfer (essentially continual swapping of electrons, bouncing back and forth) occurs between the Fe and Ti and all colours except blue are absorbed.

Other colours are generated from a combination of these elements, as well as other minor cations and defects in the crystals. Also, a single corundum gemstone can be multi-coloured from different concentrations of metals in different parts of the crystal - this is called zoning. The figure below is an example of a hypothetical crystal showing oscillatory (back and forth) zoning and a red core. You can see that the zones with Ti and Fe show up blue, those zones with no impurities are colourless, and the core with Cr exhibits red colouration.



Theoretical oscillatory zoned corundum crystal. Red region dominated by Cr, blue by Fe and Ti, while colourless has no impurities.

Some sapphires also show an optical characteristic called asterism, which is most commonly seen as a six or twelve pointed star (Lesson 13). These "arms" of the star are generated from oriented inclusions of long and skinny minerals (almost always the mineral rutile, a titanium oxide, TiO₂). Specimens found with these inclusions are often cut and polished in a rounded and polished

cabochon style to emphasize the nature of this optical effect. Rutile inclusions can occur in both sapphires and rubies, although it is more common in sapphires.

What does it look like in the rough and when cut?

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What Does it Look Like Rough?

As mentioned previously, most euhedral corundum crystals show a hexagonal growth habit forming squat plates or tapering "barrels". Often the crystals will show a modified growth habit or, if found in secondary placers, will have their delicate corners worn away. The images below show this habit with varying degrees of modification.



These two samples from Greenland occur in different geological environments which is easily seen by the different colours and textures of the "host" rocks. The rubies in the lower dark brown rock are the classic tapered barrel shape, and those in the upper white and black rock display a more unconventional blocky habit. Photo courtesy of True North Gems (http://www.truenorthgems.com/).



Close up of the above image showing the tapered barrel shape of these naturally coloured ruby crystals. The blue minerals around the rubies are kyanite, not sapphire. Photo courtesy of True North Gems (http://www.truenorthgems.com/).



The Kitaa Ruby from Greenland is possibly the largest ruby ever found in the Northern Hemisphere. This raw specimen, prior to carving, is an aggregate of intergrown ruby crystals. Photo courtesy of True North Gems ((http://www.truenorthgems.com/).



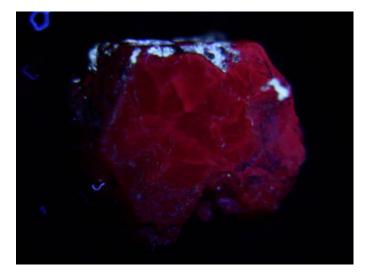
This large pink sapphire sample from Greenland shows a rough hexagonal outline of the parent mineral, corundum. Photo courtesy of <u>True North Gems</u> (http://www.truenorthgems.com/).



This large raw sapphire from Baffin Island, Nunavut shows an elongated tapered barrel shape. The smaller faceted sapphire (bottom) is untreated and from the same location. Photo courtesy of True North Gems (http://www.truenorthgems.com/).



This ruby crystal shows a rough hexagonal outline with a squat crystal form. Note the natural striations on the crystal face with intersections at ~120 degrees and the natural lichen still clinging to the stone.



This is the same specimen as above, but shown under shortwave UV light. Note the red fluorescence of the ruby and white-blue fluorescence of the lichen.

What Does Corundum Look Like When Cut?

In displaying the stone's vibrancy, the cut of sapphires and rubies is not as critical as that for diamond. However, a well planned cut will always make a stone exhibit the best possible colours and decrease the distracting presence of any inclusions. Light-coloured stones are often cut deeper to intensify colours. Deeply-coloured stones are often cut shallower in order to soften the colour. Stones that are cut too shallow display "windows" through the stone because much of the light entering will not be reflected back to the observer. If colour zoning in a specimen is present, a proper cut can hide the zoning, or if desired, emphasize it.



These polished rubies and pink sapphires from Greenland are untreated. Photo courtesy of True North Gems (http://www.truenorthgems.com/).



This vibrant pink sapphire from Greenland weighs 0.71 carats. Photo courtesy of True North Gems (http://www.truenorthgems.com/) .



These rubies and pink sapphires have an assortment of cuts and range in weight from 0.22 to 5.70 carats. Photo courtesy of True North Gems (http://www.truenorthgems.com/) .



The Kitaa Ruby from Greenland was carved from a large piece of rough ruby (88 grams, or 440 carats; shown above). After carving, it weighed a total of 302 carats. This is the front side of the carving. Photo courtesy of True North Gems (http://www.truenorthgems.com/).



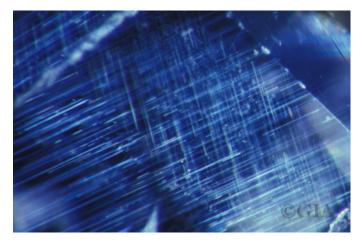
The rough and two carved sides of the Kitaa Ruby. Photo courtesy of True North Gems (http://www.truenorthgems.com/) .



The Carmen Lucia ruby, a spectacular 23.1 carat stone from Burma, is well cut and set in platinum with two diamonds. A ruby of this size and quality is extremely rare. This particular stone (and ring) is housed in the Smithsonian Institute's Janet Annenberg Hooker Hall of Geology, Gems and Minerals. Note the natural "fluid-filled" inclusion roughly in the center of this stone. Photo courtesy of the Smithsonian Institute's National Museum of Natural History (http://www.mnh.si.edu/).



Three deeply-coloured sapphires from Baffin Island, Nunavut. Photo courtesy of True North Gems (http://www.truenorthgems.com/) .



Rutile fibers (also known as "silk") in a faceted blue sapphire. These inclusions are what give rise to asterism in gemstones, which are often cut en cabochon to emphasize their star effect. Photo courtesy of the Gemological Institute of America (http://www.gia.edu/).



These two fancy yellow sapphires from Baffin Island, Nunavut originated from the same deposit as the deeply-coloured sapphires shown previously. Photo courtesy of True North Gems (http://www.truenorthgems.com/).



This black star sapphire shows typical asterism of corundum as a result of oriented rutile (TiO₂) inclusions.



Three views of an irregularly zoned sapphire from Baffin Island, Nunavut. Note that when looking at the table of the stone the colour looks well distributed, but looking through the pavillion where the light paths are different reveals how the stone is strongly zoned. The cut was designed specifically to spread the colour out in order to make it look more uniform to the observer. That takes skill! Photo and faceting by Master Cutter Brad Wilson of Alpine Gems (http://www.alpinegems.ca/index.html).

How is it recognized and distinguished from other materials?

Module B. Precious Gemstones

Lesson 18: Corundum Mineralogy and Gemology

How is it Recognized and Distinguished from Other Materials?

Corundum's hardness of 9 is distinct for this mineral, as is its hexagonal nature. However, both of these properties are more useful in the field than in the jewellery store when it is actually okay to scratch the stone! Because corundum only occurs in specific rock types with specific other minerals (see the next lesson), the geological setting can often rule out, or strengthen, the possibility of sapphire or ruby. When cut, important qualities of corundum for identification are its mineral and fluid inclusions, low dispersion, and high density.

Sapphires are sometimes confused with spinel, kyanite, benitoite, and tanzanite. Rubies are sometimes confused with garnet, tourmaline, and spinel. All of these stones are further described in your textbook, and we'll learn more about tanzanite, garnet, and tourmaline later in the course.

How is corundum valued?

Module B. Precious Gemstones

Lesson 18: Corundum Mineralogy and Gemology

How is Corundum Valued?

Rubies and sapphires are valued primarily for their colour, then for their clarity. Since rubies and sapphires are treasured for their intense colour it is no surprise that this is the primary deciding factor for its value. A nice clean stone is more attractive than one that is heavily included. Origin has a strong impact on the value of stones; size and cut are also important.

Stones originating from conflict zones or undisclosed locations are often undesirable to many consumers. Conversely, corundum sourced from historical locations are, in a sense, analogous to brand name items like Gucci or Armani. When considering size, large stones are rarer. As for cut, a poorly faceted stone will not show its best colours and will likely have to be re-cut and therefore lose some carat-weight. So, like diamonds, there are 4+1 Cs to evaluating gem corundum: colour, clarity, cut, carat... plus Country of origin!

The best sapphires are valued according to the purity and intensity of the blue, with the "ideals" showing either cornflower blue or a velvety royal blue. Most of the highest calibre sapphires come from three different regions of the world. Stones from Kashmir are often the most valuable and exhibit an intense, velvet-like blue. Burmese sapphires are also highly valued for their saturated blue. Burmese stones often show wonderful asterisms. Finally, Sri Lanka and its cornflower blues, not to mention their very large sizes, are also prized.



This photo shows a blue-violet example of the cornflower weed, the *Centaurea cyanus*. Photo courtesy of the Smithsonian Institute's <u>National Museum of Natural History</u> (http://www.mnh.si.edu/).

Rubies with Pigeon's Blood red colouration, a colour described as a pure red with a hint of blue, are highly valued. Pigeon's Blood red rubies typically originate from Burma, but other noteworthy localities of high quality ruby are found in Vietnam, Sri Lanka, and Thailand. The highest quality rubies will show a strong red fluorescence and sometimes contain fine rutile silk that scatters the light across the stone, displaying a full bodied colour. Rubies with the finest optical qualities (colour, clarity) rarely have significant weights and a stone of ~2 carats is considered quite large.

The fancy sapphires (any colour of corundum other than blue or red) are more volatile in value and are driven by the consumer market place. For instance, fancy hot pink sapphires spiked in value over the last ~5-10 years whereas colourless, yellow, green, and orange stones have not received as much attention from consumers. One exception to this are Padparadscha sapphires that have a unique orange-pink colouration. These stones are known to have prices that approach the levels of fine rubies.

Once examined by a gemologist, rubies and sapphires will be ascribed a rating based on the 4+1 Cs. Ratings for coloured stones are less comprehensive than that for diamonds, and the five usual categories used are Poor, Fair, Good, Very Good, and Exceptional. In most jewellery stores, the top stones will be of "Good" quality. Very Good stones are found in high end stores, and Exceptional stones are found only in exceptional circumstances.

Record setting prices for rubies and sapphires rival prices (on a per carat basis) of the finest diamonds. A fine Burmese ruby weighing 25.59 carats and set in a Cartier ring sold at a Sotheby's auction in 2012 for \$32.4 million USD. That works out to about \$1,267,000 per carat! An interesting quote by J.B. Tavernier (a famous historical gem trader) written in 1676 was included in the item's description for the auction. It still holds true today, almost four hundred years later:

"When a ruby exceeds 5 carats, and is perfect, it is sold for whatever is asked for it."

Of recently sold fine sapphires, a 392.52 carat Sri Lankan sapphire was auctioned by Christie's in 2014 for \$17.3 million USD, a per carat price of approximately \$44,000. A smaller (27.68 carats) but finer stone fetched about \$6.7 million USD in 2015, which is approximately \$244,000 per carat.

For more information, Richard Hughes' website __(http://www.ruby-sapphire.com/r-s-bk-quality.htm) on sapphire and rubies provides an excellent and in depth look at evaluating rubies and sapphires. It contains stunning photographs. Christie's Fine Art Auctions (http://www.christies.com/) is also a fun place to search for valuable gemstones and track down record breaking prices for fine and exceptional stones.

What are common treatments for corundum?

Module B. Precious Gemstones

Lesson 18: Corundum Mineralogy and Gemology

What are Common Treatments for Corundum?

At any gem corundum mine, most of the material found is not of gem quality. As a consequence, much effort has been directed to improving the quality of mined stones ever since mining of corundum began. Almost all (~99%) sapphires and rubies are heat treated to change colours, intensify them, and increase clarity.

The robust nature of corundum and the mineralogical changes that occur when heat treating corundum are quite favourable. The solid inclusions that detract from a stone's clarity (although some, including me, would argue that these add character to a stone) are usually comprised of elements that, coincidently, can be incorporated into corundum's crystal structure. Corundum's melting point (~2000 °C) is higher than most of its common inclusions, thus heating allows the solid inclusions to resorb or "melt" back into the corundum's crystal structure without melting the corundum.

Heating improves clarity by "removing" the opaque solid inclusions, but also by allowing chromophore-type elements within those inclusions, such as Ti and Fe, to become part of the corundum crystal and help colour the stone. Under the right conditions, Fe can be chemically "persuaded" to acquire a charge of either +2 or +3 which will also affect the resulting colour. Other types of inclusions won't add to a stone during heat treatment, but these features can be annealed or healed to make them "disappear". Consequently, the clarity of the treated stone can increase dramatically.

Corundum also commonly undergoes diffusion treatment where an element not associated with the crystal is forced into the structure via heat, pressure, and chemical gradients. This allows the "treater" or chemist, to impart a variety of colours to the original crystal. Diffusion is most commonly used to change colourless sapphires into Padparadscha sapphires.

Treatment to corundum is typically done to rough stones that have not yet been cut since exposure to the high heat can also cause new fractures to form. Otherwise, a faceted stone could lose

considerable value if it broke during the heat treatment process.





"Before" (left) and "after" (right) example of heat treatment on rough sapphire The Natural
SapphireCompany
(http://www.thenaturalsapphirecompany.com/).

Can corundum be produced synthetically? What are its imitations?

Module B. Precious Gemstones

Lesson 18: Corundum Mineralogy and Gemology

Can Corundum be Produced Synthetically?

Due to its simple chemical makeup, corundum has been produced synthetically since 1837 and gem quality synthetic corundum entered the marketplace in the early 1900's. All colours can be produced synthetically, and very large sizes (more than 100 carats!) can also be achieved using Czochralski's Drawing Method. This process involves taking the necessary oxide components for gem corundum (e.g., Al₂O₃, Fe₂O₃, TiO₂, Cr₂O₃) in powdered form and melting them together in a hot container that is just barely over the crystallizing temperature. A rod with a small corundum seed crystal is lowered into the molten material and then very slowly removed. As the crystal is raised above the nutrient rich molten mixture a small amount of corundum is formed at the interface between the seed crystal and the molten mixture. As the rod is slowly pulled upwards, new corundum continually grows below!

Another common technique for growing synthetic corundum is called the Vernueil Process and involves "dripping" of melted corundum onto bulb shaped corundum crystal. This process is similar to how stalactites form in caves.

Luckily, even the best synthetic corundum crystals will show signs of their history by specific identifiable (but often only to trained gemologists) inclusions related to their growth. Synthetic stones, as expected, are considerably cheaper than natural stones.

What are its Imitations?

Imitation sapphires and rubies have always been around, often times by accident. Prior to robust testing and mineralogical identification, many spinels and garnets were actually thought to be rubies. Mistaken identifications have also been made with sapphires, the most common being kyanite, blue glass, and topaz. As expert identification became more commonplace and prominent

in the 1800's, these "misidentified" stones migrated to the "imitation" category when being sold as rubies or sapphires. Today, most of these stones are considered gem varieties in their own right.

Today, imitations for sapphires and rubies are mostly in the form of doublets where natural colourless sapphire/corundum has a coloured synthetic corundum crystal glued underneath. Other composite constructions also exist and can be difficult to identify even with the proper gemological tools.

Review Lesson 18

Module B. Precious Gemstones

Lesson 18: Corundum Mineralogy and Gemology

Review and Check Your Understanding

Learning Objectives

- 1. Use the diagnostic properties of corundum (e.g., hardness, refractive index, SG, habit, cleavage, fluorescence) to identify it.
- 2. Compare the physical properties of corundum to other gems we have studied thus far.
- 3. Describe the mineral formula and crystal structure of corundum.
- 4. Explain the differences between the different gem corundum varieties (e.g., ruby, sapphire, fancy sapphire, corundum with asterism).
- 5. Describe the main variables used to value gem corundum.
- 6. Identify common treatments and imitations of gem corundum.

Review

- What is the chemical formula of corundum?
- · Why corundum can be found in a wide variety of colours?
- In particular, what gives rise the "Pigeon's Blood Red" and "Cornflower Blue" colours in corundum?
- What minerals are rubies commonly confused with? What about sapphires? How could you tell rubies and sapphires apart from some of these common "imitation" minerals?
- Compare the hardness, cleavage, specific gravity, crystal system and refractive index (or indices) of corundum to diamond and beryl. (Use your physical properties summary sheet!)