The Fingerprint File
GEM IDENTIFICATION

This is the second of a two part series by Kirk Feral where he investigates the roles chromium and vanadium play in the colouration of gems and how their presence can be detected.

Masters of Green: Chromium and Vanadium (Part Two)

Detecting Chromium and Vanadium

So how do we detect chromium or vanadium in gemstones, and how do we distinguish between them? In my own lab, basic tools include a Chelsea color filter, a long wave UV flashlight (365nm), a blue laser (405nm), a dichroscope and a hand-held spectroscope. The absence of any chromium response to these tools in some instances indicates that vanadium rather than chromium is the dominant cause of color. A magnetic wand is also part of my arsenal of equipment. I rely on a UV-Vis-NIR spectrometer as a more definitive tool for detecting chromium and vanadium and for distinguishing between them.

Tools for Detecting Chromium & Vanadium

I find that a handheld spectroscope is of limited use in detecting chromium in natural green gemstones such as jadeite, chrome chalcedony and demantoid garnet. Black absorption lines indicative of chromium may be present in the red/orange region of the spectrum, but these lines are often very difficult to see against the dark red background unless the concentration of chromium in a gem is particularly high, as we find in some synthetic emeralds and some dark green natural emeralds.

Similarly, because the concentration of chromium and vanadium in most natural green gems is very low, an N52 neodymium magnet is seldom able to detect the magnetic susceptibility of these two metallic chromophores. Moderate to strong magnetic responses in natural green stones colored by chromium and vanadium is usually an indication of iron content.

A dichroscope can occasionally be helpful in confirming the presence of chromium in a doubly refractive green gem. When pink color is seen along with green color under a dichroscope, the pink color component is usually indicative of chromium. We encounter pink/green dichroism in green chrysoberyl gems, hiddenite, vanadium diopside and some emeralds. But such dichroism involving chromium is not apparent in other green chromium-bearing gems such as chrome tourmaline, chrome diopside, chrome sphene, singly refractive gems or microcrystalline gems.

Chelsea Filter

To detect chromium, a Chelsea filter is one of the most useful tools. When incandescent light is applied to a green gemstone that is viewed under a Chelsea filter, the presence of chromium is indicated when the gem appears pink or red rather than green. I know of only 3 exceptions to this rule:

- Blue-green synthetic spinel: a red Chelsea filter reaction is due to cobalt.
- Green zircon: a red reaction is due to color centers that are unrelated to chromium.
- Green sphene: a red reaction is likely due to rare earth elements or possibly iron rather than chromium. Yellow and brown sphenes that have no chromium or vanadium show similar red reactions.

Vanadium does not produce a red reaction to a Chelsea filter, and this fact can be helpful for separating gems colored by chromium from those colored by vanadium. However, it's important to know that in some cases gemstones such as 'chrome' tourmaline that are colored primarily by vanadium can still appear pink or red under the filter if any consequential amount of chromium is also present. Vanadium does not suppress red Chelsea filter reactions caused by chromium.

Strong red Chelsea filter reactions by green gemstones typically indicate relatively high levels of chromium. Conversely, extremely low concentrations of chromium may be insufficient to cause a red reaction under a Chelsea filter. Among gems that I've tested, light green hiddenite gems from Brazil colored by chromium along with vanadium show no red Chelsea filter reaction, undoubtedly because so little chromium is present.

As luck would have it, iron (Fe^{2+}) does suppress red Chelsea filter reactions. The level of suppression is dependent on the ratio of iron to chromium, as well as the total amount of iron and chromium in a gem.

If a gem shows just a faint pink reaction or remains green under the Chelsea filter, this doesn't necessarily mean that chromium levels are low or absent. Instead, iron could be suppressing the red reaction. For instance, iron is usually present in natural emeralds, and consequently many natural emeralds colored by chromium remain green under a Chelsea filter instead of appearing pink or red.

As another example, fine translucent jadeite or 'imperial' jade is colored green by a combination of iron and chromium. But due to suppression by iron, jadeite shows no red Chelsea filter reaction from chromium. The same is true of chrome diopside and chrome enstatite gems, which also derive color from chromium and iron.

Jadeite (Iron & Chromium)

A Chelsea filter can still be useful for testing jadeite. If a red Chelsea filter reaction is apparent in jadeite, this is a sure indication that the stone has been treated with a green dye or polymer that contains chromium. Unfortunately, not all treated jadeite can be detected with a Chelsea filter, as jadeite is often treated with vegetable dyes or polymers that aren't chromium-based.

Other translucent or opaque green cabochon gems that may look like jadeite include hydrogrossular garnet, variscite, dyed chalcedony and dyed hydrophane opal. These green gemstones often contain chromium and can often be distinguished from untreated jadeite by a red reaction to a Chelsea filter.

An interesting example of iron that fails to suppress red Chelsea filter reactions is trivalent iron (Fe^{3+}) in tsavorite grossular garnets and demantoid andradite garnets. Chromium is readily detected in these green garnets with a Chelsea filter even when the iron content is extremely high, as we find in demantoid garnets.

Demantoid Garnet (Iron & Chromium)

'Chrome' tourmalines belong to the dravite species. Although they are mostly colored by vanadium, 'chrome' tourmaline gems always contain some amount of chromium and show a pink or red chromium reaction under a Chelsea filter. This reaction can be used to separate 'chrome' tourmalines from the more common 'verdelite' tourmalines of the elbaite species, which are colored green by iron. Verdelite remains green under a Chelsea filter.

The color of 'chrome' tourmalines is typically dark green, but on occasion these gems can have moderate to light green color. The lighter color of these tourmalines is due to lower concentrations of vanadium and chromium. These unusual gems show only a weak pink reaction under a Chelsea filter as a result of the low level of chromium.

Yellow-Green Chrome Tourmaline

UV Flashlight

Chromium is a strong activator of fluorescence in gems, and a high-quality longwave 365nm UV flashlight or longwave UV lamp is an important tool for detecting the presence of chromium. Chromium fluorescence in transparent and translucent gemstones is stronger under longwave UV light than under shortwave UV light.

Whenever a green gemstone fluoresces red or pink under longwave UV light, chromium is indicated, and very strong red fluorescence is often an indication of a high concentration of chromium. The one key exception is synthetic bluish green spinel, which fluoresces red due to cobalt rather than chromium.

Vanadium is not known to be a fluorescence activator, and it never causes red fluorescence. Yellow fluorescence in light green 'chrome' kornerupine gems and light green vanadium diopside gems colored by vanadium is probably due to manganese rather than vanadium.

Unique among gemstones is man-made iron-free glass colored green only by chromium (Cr^{3+}). Even when a significant amount of chromium is present (1.0 %), chromium glass is inert to longwave UV light. Apparently chemical interactions within glass inhibit red chromium fluorescence, and any red reaction under a Chelsea filter is also suppressed.

In natural gems, the presence of chromium is not always revealed through red fluorescence. A green gem that shows no UV fluorescence can still have chromium as the primary cause of green color. For instance, most emeralds, natural or synthetic, don't fluoresce under longwave UV light. There are two important reasons for this.

- iron can reduce or completely quench the red fluorescence of chromium, as it does with red Chelsea filter reactions.

- vanadium is also a powerful quencher of fluorescence, and it can quench the red fluorescence of chromium at least as effectively as iron. This important fact is not generally recognized in gemology.

Some emeralds do fluoresce pink or red from chromium, but only when they contain very little iron and very little vanadium. Such emeralds also show pink & green dichroism under a dichroscope due to chromium.

Most natural emeralds don't fluoresce because they are colored by a mixture of chromium, vanadium and iron. Synthetic emeralds that are free of iron don't fluoresce due to the presence of vanadium, which inhibits chromium fluorescence.

When chromium is revealed in any type of gem by a red reaction to a Chelsea filter, but no concomitant UV fluorescence is apparent, we can safely assume that the chromium fluorescence is being quenched by vanadium. Most 'chrome' tourmalines that I've tested are red under a Chelsea filter, but they show no chromium fluorescence under longwave UV light due to quenching by vanadium.

This quenching effect may indicate that vanadium is present in higher concentrations than chromium, as in most 'chrome' tourmalines. But I've found that in some emeralds, quenching of chromium fluorescence by vanadium can occur even when chromium is the dominant cause of color.

Green garnets colored by vanadium and chromium are quite interesting in their reaction to UV light. Dark green grossular garnets such as tsavorite gems and 'chrome' Mali garnets show little or no chromium fluorescence due to quenching by vanadium, the dominant chromophore. But lighter green grossular garnets such as 'Merelani' garnets typically do show pink fluorescence from chromium. This increased fluorescence suggests that the lower concentration of vanadium in the lighter grossulars is insufficient to quench the fluorescence.


Dark Green 'Chrome' Mali Garnet & Light Green Merelani Garnet

Another interesting point is that these light green garnets show pink and red UV fluorescence in the presence of iron. Fluorescence is possible in grossular garnets due to the relatively low concentration of iron. Also, the type of iron found in grossular and andradite garnets is mostly trivalent (Fe^{3+}), which is much less efficient at quenching fluorescence than divalent iron (Fe^{2+}). The much higher concentration of iron found in green demantoid garnets (andradite species) does quench chromium fluorescence completely.

In any type of green gem, when the concentration of chromium is extremely low, the chromium may be insufficient to induce pink or red fluorescence under UV light. This is the case with some greenish yellow chrysoberyl gems that contain only trace amounts of chromium (less than 0.1% chromium oxide). A greater amount of chromium (still under 1.0%) as we find in green chrysoberyl and alexandrite chrysoberyl results in strong red fluorescence.

At the other extreme, a very high concentration of chromium can quench all UV fluorescence, as is evident in uvarovite garnet, an idiochromatic gem that can contain over 25% chromium oxide. This phenomenon is referred to as concentration quenching. Among green gems that are allochromatic, the level of chromium oxide rarely reaches 2%, a concentration that's probably too low to have any quenching effect on fluorescence.

Magnetic Wand

The only natural green gemstone that shows a strong attraction to a magnetic wand due to chromium is uvarovite garnet. Among man-made green gems, some synthetic emeralds are strongly magnetic due to high concentrations of chromium and vanadium.

Strong attraction to a magnetic wand by a natural green gem usually indicates the presence of iron rather than chromium or vanadium. In some cases, a strong magnetic response can alert us that sufficient iron is present to quench any fluorescence or red Chelsea filter reaction from chromium. As examples, chrome diopside and chrome enstatite gems colored green by chromium don't appear red under a UV light or a Chelsea filter due to the inhibiting effect of magnetic iron.

Like the Chelsea filter, a magnetic wand is a handy tool for separating 'chrome' tourmalines from other green tourmalines. 'Chrome' tourmalines (dravite species) are diamagnetic, or occasionally very weakly magnetic, because they contain almost no iron. In contrast, green tourmalines of the elbaite species contain enough iron to cause significant magnetic attraction to an N52 neodymium magnet. Dark green 'verdelite' tourmalines typically show a drag response.

'Chrome' Tourmaline & Verdelite Tourmaline

Blue Laser

An inexpensive blue laser pointer is an indispensable tool for revealing the presence of chromium. Like a longwave UV light, a blue laser causes pink or red chromium fluorescence. A blue laser employs a concentrated beam of violet light that's barely within the visible range (405nm) and just above the UV range.

This tool is so sensitive that it can reveal trace amounts of chromium even when the concentration is too low to be detected with a high-quality UV flashlight or lamp. In addition, fluorescence under a 405nm laser can reveal the presence of chromium even when iron or vanadium completely quenches fluorescence under UV light.

A blue laser is also more sensitive than a Chelsea filter, revealing chromium in a gem when the concentration is too low to cause a red Chelsea filter reaction. As an example, light green spodumene (hiddenite) gems from Brazil are colored by small amounts of chromium. These hiddenite gems don't show a red Chelsea filter reaction or UV fluorescence from chromium, but chromium can be detected by red fluorescence under a blue laser.

It's important to remember that when we don't see any UV fluorescence in a green gem, nor any fluorescence from a blue laser, nor any red reaction to a Chelsea filter by that gem, chromium can still be present within the gem. Chromium might even be the primary cause of color. The chromium may simply be hidden from detection by a substantial amount of iron.

Strategic use of basic tools such as a blue laser, UV flashlight, Chelsea filter, magnetic wand, dichroscope and spectroscope can help us confirm or eliminate chromium and vanadium as possible causes of green color in a gem, or point toward another possible chromophore such as iron (ex. peridot) or nickel (ex. chrysoprase). But at times we must rely on a UV-Vis-NIR spectrometer to verify the presence of chromium or vanadium, or to distinguish between these two chromophores.

Spectrometer

A spectrometer that spans the ultraviolet, visible and near-infrared range of light is a much more sensitive instrument than a hand-held spectroscope. Absorption spectra as seen with a spectrometer are made up of peaks and valleys, with the peaks corresponding to black lines and bands seen with a spectroscope.

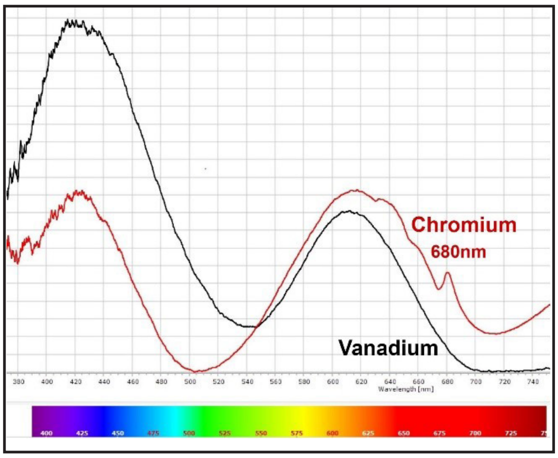
The absorption spectra produced by vanadium are very similar to the spectra of chromium, another confirmation that green colors produced by each chromophore are very similar to each other. A broad absorption peak in the blue region and another in the red region of the visible spectrum indicate that most of the blue and red light is absorbed, leaving a broad valley in the middle of the spectrum where only green light is transmitted, causing green gem color.

In the spectra for both chromium and vanadium, light transmission through the green region near the center of the spectrum can also extend a bit toward the left or right of center. For example, if some light is also transmitted from the blue region to the left, the result is blue-green gem color.

In other gems, some light might be transmitted from the yellow region to the right, and yellow-green body color is the result. These variations in color are seen in the spectra for both chromium and vanadium.

The most characteristic difference between a chromium spectrum and a vanadium spectrum in a green gem is a sharp absorption peak produced by chromium near the 680nm wavelength at the upper limit of the red region of the visible spectrum. The position of this chromium peak can vary from approximately 670nm to 690nm depending on the type of green gem.

The sharp 680nm peak and other less conspicuous peaks near 650nm, 630nm and 600nm are typical of chromium and are never produced by vanadium. The absorption pattern produced by vanadium in the red region of the spectrum is smooth with no sharp peaks.



Spectrometer Absorption Spectra
for Chromium & Vanadium

The 680nm peak produced by chromium is actually a combination of two very closely aligned peaks known as R lines. When the concentration of chromium within a green gem is high, these R lines are also visible with a handheld spectroscope as a chromium doublet of two black lines.

Whenever we see red UV fluorescence from chromium in a green gem, that fluorescence is the result of red light being transmitted precisely at the R lines (and on into the infrared spectrum). Vanadium lacks R lines in its absorption spectrum and fails to cause UV fluorescence.

We can approximate the amount of vanadium in a gem relative to the amount of chromium by looking at the gem's absorption spectrum rendered by a UV-Vis-NIR spectrometer. There are 3 basic variations of the absorption spectrum that give us clues about the proportions of chromium to vanadium.

- When a green gem is colored primarily by chromium, the absorption peak at 680nm is in most cases clearly visible, even when a lesser amount of vanadium is also present.
- When a green gem is colored green primarily by vanadium, it has a smooth spectrum with no chromium peak at 680nm, even though some amount of chromium may also be present.
- When chromium and vanadium are roughly equal in concentration, contributing equally to green color, just a slight curvature or bump at 680nm may be apparent.

Even with the aid of a spectrometer and all our other instruments, determining whether chromium or vanadium is the primary cause of gem color can at times be difficult, and accurate measurements of the relative percentages of chromium and vanadium are generally not possible. More quantitative measurements of these two chromophores require much more sophisticated and costly methods that can analyze the chemical composition of a gem. Such methods include energy dispersive x-ray fluorescence (ED-XRF), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and electron probe microanalysis (EPMA).

Emerald and Green Beryl

The world's most valuable green gemstone is emerald, which is a variety of beryl colored by chromium, vanadium and iron. The word 'emerald' is an ancient trade name rather than a scientific one, and so disagreements arise about exactly what constitutes an emerald and what differentiates an emerald from other green gems of the beryl species. Color saturation is one criterion used to classify emerald. The color of emerald beryl actually varies from light green to dark green. Unfortunately, most gemologists ally themselves with tradition rather than science, classifying only moderate green to dark green gems as true emeralds.

Dark Green & Moderate Green Emerald

So, what do we call an emerald with light green color? Well, 'light green emerald' would be a good choice, but these gems are often referred to by gemologists as green beryl. This nomenclature creates confusion, as the name 'green beryl' generally refers to a variety of beryl colored green by iron. The distinctive olive green or yellow-green color of green beryl is the result of a combination of bivalent iron

(Fe^{2+}) and trivalent iron (Fe^{3+}) rather than chromium and vanadium. Green beryl gems also generally have better clarity than emeralds.

Light Green Emerald (Chromium) & Green Beryl (Iron)

Another point of confusion over what constitutes an emerald is whether it is colored by chromium instead of vanadium. An antiquated notion persists among some gemologists that a beryl colored mostly or entirely by vanadium must be classified as a green beryl rather than an emerald.

This is a bit of nonsense, as chromium and vanadium create similar green colors in beryl. Some synthetic hydrothermal emeralds with spectacular green color are doped entirely by vanadium, and based on appearance, no gemologist would classify these gems as green beryl.

In most natural emeralds, chromium and vanadium occur together in varying proportions, and iron is also usually present as a color modifier. Although chromium is usually the primary chromophore in natural emeralds, some natural emeralds are colored mostly by vanadium.

Colombian Emeralds Colored Primarily by Chromium (Left) and Vanadium (Right)

Of the synthetic emeralds that I've examined, those colored primarily by vanadium appear slightly lighter and slightly bluer in color than gems colored primarily by chromium.

Synthetic Emeralds Colored Primarily by Chromium (Left) and Vanadium (Right)

Among natural emeralds, the amount of iron within a gem is a more relevant factor to the quality of color than the amount of vanadium.

Divalent iron (Fe^{2+}) creates the blue color of aquamarine beryl, and small amounts of divalent iron in emerald can add a blue tint to the green color produced by chromium and vanadium.

The blue color component common in many natural emeralds, particularly in emeralds from Zambia, is due mostly to iron rather than to vanadium. In contrast, when enough iron is in the trivalent oxidation state (Fe^{3+}), the iron can add a yellowish hue to an emerald.

Blue-Green Emerald & Yellow-Green Emerald

The most valuable emeralds in the world are generally mined in Colombia, but fine emeralds are not exclusive to that country. They can also be found in Brazil, Zambia, Ethiopia and other regions of the world. Whatever the origin, the beauty and value of an emerald generally corresponds with the saturation or strength of green color.

Colombian emeralds show some of the most desirable green colors precisely because they are so low in iron compared to emeralds from other parts of the world. In many Colombian emeralds, color is entirely the result of chromium and vanadium.

My own study of magnetism in beryl gems indicates that the low level of iron found in many emeralds from Colombia is insufficient to have any effect on body color. In the rare instance that an emerald is diamagnetic and additionally shows no red reaction to a Chelsea filter, we can be confident that vanadium is the sole cause of green color.

Fine Colombian emeralds that have dark green color due to high levels of chromium will fluoresce red in UV light when vanadium and iron levels are too low to quench fluorescence. Red fluorescence in daylight is also possible, much like the daylight fluorescence of some rubies. This daylight fluorescence is not readily apparent to the eye, but it may add vibrance to the appearance of an emerald.

‘Vanadium emerald’ is a term currently being applied to some light greenish blue beryl gems from Nigeria. This trade name is problematic, in part because these gems are too blue to be classified as emeralds, and also because vanadium is not the cause of the blue color.

The high proportion of blue color in these ‘vanadium emeralds’ is caused by iron. Other trade names assigned to these beryl gems include vanadium beryl, green beryl and Nigerian emerald.

When the color of a beryl gem is equal parts blue and green, as it is in the ‘Nigerian emeralds’ that I’ve examined, the gems look like unheated aquamarine. The light blue color component is due to traces of divalent iron (Fe^{2+}), while the light green color component is derived from trace amounts of both chromium and vanadium. These gems can be accurately regarded as an intermediary between aquamarine and emerald, and a more appropriate name for such a hybrid would be ‘chromium-bearing aquamarine’.

Chromium-bearing Aquamarine

Besides chromium-bearing aquamarine, I was surprised to find that some green beryl gems are also colored partly by chromium and vanadium in addition to iron. This iteration of beryl can be called chromium-bearing green beryl. I have not seen these two intermediary color varieties described anywhere else.

A familiar and well-documented color gradation in beryl involves varying proportions of trivalent iron to bivalent iron, with a progression from yellow beryl to green beryl to aquamarine. Results of my own study of beryl gems reveal that a separate but related gradation or continuum of color exists between green beryl, emerald and aquamarine. That continuum involves the presence or absence of chromium and vanadium in relation to iron.

This new continuum in beryl progresses as follows: green beryl colored only by iron → yellowish green chromium-bearing green beryl → emerald colored by chromium, vanadium and iron → greenish blue chromium-bearing aquamarine → aquamarine colored only by iron. Differences in color between these gradations can be subtle, and color alone may not reveal the presence of chromium/vanadium within intermediary gems.

Green Beryl → Chromium-bearing Green Beryl → Emerald → Chromium-bearing Aquamarine → Aquamarine

A curious example of an imitation emerald that had me scratching my head for a bit is a heavily fractured gem colored green by chromium. At first glance, the gem looks much like a light green heavily included emerald. It also shows a chromium absorption spectrum like that of natural emerald.

But a refractive index of 1.76 -1.77 and a thermal inertia reading of 48 identify this gem as corundum. It’s a clever imitation, but what’s puzzling is that chromium can only create red or pink color in corundum, as we see in ruby and pink sapphire. So how can this corundum gem be green?

The likely explanation is that this gem is a quirky example of a natural glass-filled corundum. Green color was likely imparted when the multiple fractures within a low-quality piece of natural corundum were flushed with acid and then filled with glass colored green by chromium.

Natural Corundum Filled with Chromium Glass

Another example of green chromium-bearing corundum that might pass for emerald are some green synthetic corundum gems. In synthetic corundum, blue-green color can be achieved by combining chromium with another dopant, nickel. Again, chromium doesn't cause green color in corundum. In this case, light green color is created by trace amounts of nickel in 2 different oxidation states: blue color from bivalent nickel (Ni^{2+}) mixes with yellow color from trivalent nickel (Ni^{3+}) to create the green color.

Synthetic Corundum Colored by Chromium & Nickel

In such gems, a light pink color component derived from chromium modifies the saturation and tone of the green gem without adding pink body color. However, the two distinct color components, pink and green, are revealed with a dichroscope. The chromium in these unusual synthetic corundum gems is also detected as pink color under a Chelsea filter, as pink fluorescence under long wave UV light, and as a chromium absorption spectrum under a spectrometer.

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