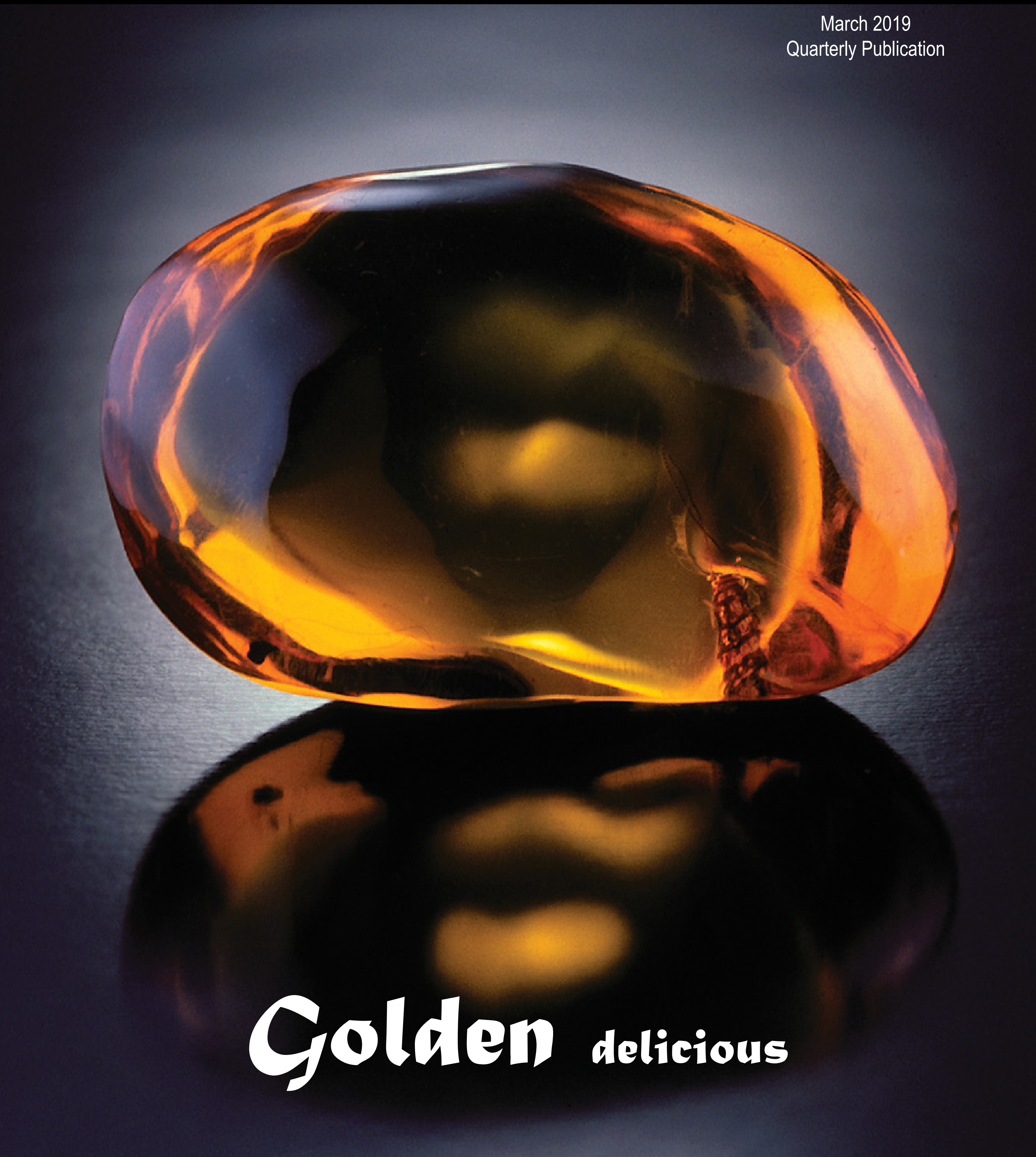
Gemmology Today

March 2019
Quarterly Publication



Golden delicious

The Fingerprint File GEM IDENTIFICATION

This is the first part 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

The Dynamic Duo

Chromium and vanadium are metallic elements that often act together as chromophores or coloring agents in gems and minerals, creating a green color. Other metals such as iron and copper can also create a green color, but chromium and vanadium produce some of the most spectacular green hues found in gemstones.

The name for chromium was derived from the Greek word chroma, which means color. Chromium can produce red color in gems such as ruby and spinel, and green color in gems like emerald and fine jade. The terms ‘ruby red’ and ‘emerald green’ are affiliated with royalty and represent ideal versions of color that have been held for centuries, primarily due to the element chromium.

By virtue of this long heritage, chromium gets all the credit for the best green colors and is by default the king of green in the mineral kingdom. But if chromium is king, then vanadium is truly the queen of green.

Vanadium is named after Vanadis, the ancient Scandinavian goddess of beauty. Like chromium, vanadium also produces stunning green colors that range from delicate light green to rich dark green. On occasion vanadium also creates blue color, as we find in tanzanite and cavansite.

Because vanadium is often less familiar than chromium and less understood as a cause of green color in gems, it’s regarded somewhat as a stepchild to chromium. But as we shall see, the role of vanadium in creating vibrant green color rivals that of chromium.

Emerald (Chromium) & Tsavorite Garnet (Vanadium)

Chromium and vanadium are among the 25 most abundant elements within the earth’s crust. For use in industrial alloys, these two metals are mined from ores such as chromite (chromium) and magnetite (vanadium).

On the Periodic Table of Elements, chromium and vanadium have the atomic numbers # 23 and # 24 and are arranged side by side in the first row of transition metals. When ions of chromium and vanadium are dissolved in solid solution within gemstones, the ions combine with oxygen to form oxides that give rise to green color: chromium oxide (Cr_2O_3) and vanadium oxide (V_2O_3). Undissolved chromium oxide takes the form of a pure green powder.

Chromium Oxide

The chromium and vanadium ions found in these metal oxides exist in the trivalent oxidation state: Cr^{3+} and V^{3+}. Trivalence simply means that each atom has gained a positive charge of 3 after losing 3 electrons when binding with oxygen. Depending on the type of mineral, trivalent chromium can produce either green color or red color. Trivalent vanadium results only in green color in gems, except for zoisite (tanzanite), in which V^{3+} can also produce brown, violet and possibly blue color.

Other valence states of chromium and vanadium create different colors, but these rarely occur among gems and minerals. Quadrivalent vanadium (V^{4+}) within vanadium oxide (VO^{2+}) creates the bright blue color in the mineral cavansite.

Hexavalent chromium (Cr^{6+}) creates an intense orange color in the mineral crocoite, but in man-made pigments it produces a yellow color. Chrome yellow paint (lead chromate) was common in artist palettes, taxi cabs and school buses until it was determined to be toxic.

Deconstructing Green Color

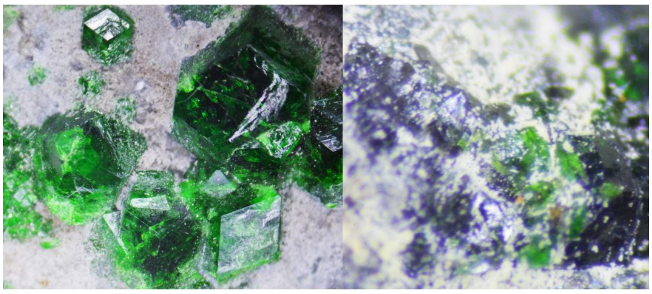
The single most important factor that determines the value of any colored stone is color, and gems with the strongest color generally are the most desirable and command the highest prices. The quality of green color in gemstones in terms of hue, tone and saturation is undoubtedly examined more fastidiously in emeralds than in any other type of gem. Chromium and vanadium almost always occur together as a pair to create green color in emeralds and all other types of green gemstones, and the proportion of chromium to vanadium can vary widely. Gems colored mostly by vanadium can be indistinguishable in color from gems colored mostly by chromium.

The colors produced by chromium and vanadium range in saturation from light to dark, and in hue from blue-green to pure green to yellow-green. With the aid of a dichroscope, we can at times see dichroism within a single gem that reflects these variations in green color: green & blue, or green & yellow.

It's difficult to know precisely how each chromophore by itself affects the color of a single green gem. Does vanadium create exactly the same green color as chromium? The answer is stubbornly elusive, and no information has been published that definitively answers this fundamental question.

We can attempt to find the answer ourselves by looking at examples of natural green gemstones that are colored only by chromium and only by vanadium. Such examples are rare in nature. The nearest approximations of minerals colored entirely by chromium are natural crystals of the uvarovite species of garnet, and also crystals of the chromium-dravite species of tourmaline. The concentration of chromium oxide in these minerals can be as high as 30%, making the crystals opaque. Uvarovite and chromium-dravite both show a dark pure green color.

Two species of mineral colored almost exclusively by extremely high concentrations of vanadium are idiochromatic goldmanite garnet and vanadium-dravite tourmaline. Near-opaque crystals of these vanadium minerals also show a dark pure green color, and can be nearly identical in hue, tone and saturation to crystals with very high concentrations of chromium. So, we know that chromium and vanadium are each capable of creating a pure green color when present in high concentrations within natural idiochromatic minerals.



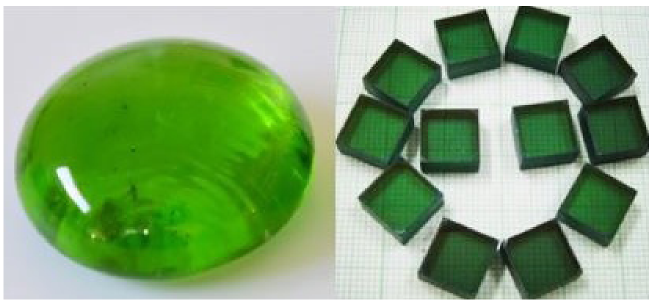
Uvarovite Garnet (Chromium) & Goldmanite Garnet (Vanadium)

Much lower concentrations of chromium and vanadium are found in allochromatic gemstones. To observe the effect of a low concentration of chromium or vanadium on the color of a gem, with no influence from any other coloring agent or impurity, we must turn to lab materials that are manufactured under controlled conditions.

Lab-created materials colored green by only one dopant (coloring agent) are nearly as hard to find as natural gems colored by a single chromophore. For example, most synthetic emeralds contain both chromium and vanadium. Additionally, iron or copper may also be added to synthetic emeralds to modify their emerald color.

I was able to locate a specialty glass colored green exclusively by chromium (Cr^{3+}), and also an industrial YAG (yttrium aluminum garnet) colored green only by vanadium (V^{3+}). These transparent materials contain no other dopants that might affect color.

It turns out that barium phosphate glass doped with 1% chromium shows a bright green color that is slightly yellowish. YAG doped only with vanadium for use in solid-state lasers shows a dark green color that appears slightly bluish. But these are 2 different host materials. A better comparison would be chromium YAG to vanadium YAG, but most chromium YAG is manufactured with thulium and holmium, which can alter the color.



Chromium Glass & Vanadium YAG

The story of color produced by chromium and vanadium in natural allochromatic gemstones is much more complex than what we find in the lab. In most natural gems, does vanadium create a blue-green color, while chromium imparts a yellow-green color? Can the opposite be true? Does vanadium create a darker green color than chromium, or vice versa? The short answer is that the kind of green color caused by chromium or vanadium varies with the type of gem and with the concentration of the chromophore. My own observation is that a blue-green color and a light color saturation are both associated more often with vanadium than with chromium in natural transparent gemstones.

Researchers have established that the higher the concentration of chromium and/or vanadium within a gem, the darker the green color. Published microprobe data showing the measured amounts of chromium and vanadium that produce various levels of color saturation in gems suggest that vanadium has the potential to create a strong green color as readily as chromium. Just a trace amount of chromium or vanadium oxide (less than 0.1% by weight) can cause a light green color in some gemstones, and one percent (1.0%) produces a dark green color.

To better understand how each chromophore individually affects color, we can compare examples of allochromatic gems and minerals that are colored primarily by either chromium or vanadium. In many varieties of green gems, vanadium is the dominant chromophore.

We will assume that the leading cause of color in any green gem is the coloring agent with the greatest concentration. Below is a table showing a partial list of gems that derive green color mostly from chromium or mostly from vanadium.

Chromium Dominant	Vanadium Dominant
Chrome Diopside	Tsavorite Garnet
Chrome Chalcedony	Chrome Tourmaline
Chrome Enstatite	Chrome Kornerupine
Most Emeralds	Chrome Mali Garnet
Alexandrite Chrysoberyl	Chrome Sphene
Demantoid Garnet	Hydrogrossular Garnet
Uvarovite Garnet	Vanadium Chrysoberyl
Hiddenite Spodumene	Vanadium Diopside
Some Jadeite	Zoisite

Not included in this table are other gems that can be colored green by a combination of chromium and vanadium, such as kyanite, prehnite, variscite, amblygonite and vesuvianite.

Natural gemstones that are vanadium-dominant are often associated with blue-green colors. Light blue-green 'Merelani' grossular garnets and the light blue-green vanadium chrysoberyl derive their color primarily from vanadium, but chromium is also present.

However, a blue-green color can also be associated with chromium-dominant gems, as we see in some iron-free emeralds and some chrome chalcedony gems.

Vanadium Chrysoberyl & Chrome Chalcedony (Chromium)

Vanadium is also associated with a yellow-green color in some gemstones. As an example, vanadium diopside usually has a yellow-green color.

A green color with a slightly yellowish hue is also seen in some gems colored mostly by chromium, such as some light green hiddenite gems (spodumene).

Vanadium Diopside & Hiddenite (Spodumene)

A dark green color in natural gemstones is often associated with chromium, as we see in the voluptuous colors of chrome diopside and chrome demantoid garnet. But similar dark pure green colors can also be found in gems colored primarily by vanadium, as we see in the dazzling colors of tsavorite garnet and 'chrome' tourmaline.

Chrome Diopside (Chromium) & 'Chrome' Tourmaline (Vanadium)

Demantoid Garnet (Chromium) & Green YAG (Vanadium)

Lower concentrations of either chromium or vanadium can result in light green colors. Light green demantoid garnet colored by chromium along with iron can be indistinguishable with the naked eye from light green man-made YAG colored by vanadium.

'Vanadium' Dravite

'Chrome' Tourmaline

Finally, let's look at the color of a rare example of a transparent faceted vanadium-dravite tourmaline, which is idiochromatic and colored by a high concentration of vanadium. Compared to the color of allochromatic 'chrome' tourmaline caused by much less vanadium along with some chromium, the vanadium-dravite color is slightly bluer.

Modified Green Color

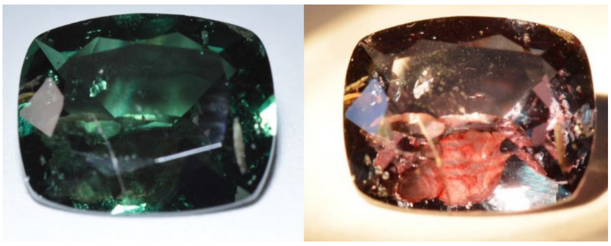
All the above examples suggest that slight modifications to a green color away from pure green toward blue-green or yellow-green is linked not only to the ratio of chromium to vanadium, but also to the chemical composition and crystal structure of the host mineral in which the chromium and vanadium is found.

'Chrome' Sphene (Vanadium)

Chrome Enstatite (Chromium)

Green color from chromium and vanadium can also be modified by the presence of an additional chromophore. For example, in chrome' sphene (titanite), iron and/or rare earth elements can give a yellowish or brownish hue to the green body color created by vanadium and chromium.

High iron content and/or charge transfer processes involving iron may darken the tone of some gemstones colored by chromium, as we find in chrome diopside and chrome enstatite gems.



Color Change Garnet in Daylight and Incandescent Light

Variations in the light source can also modify the color of a gem. A cool LED light can modify the color of a green gem in daylight toward blue, while warm incandescent lighting can shift the green color toward yellow. In color-change gems such as alexandrite and color change garnet, the presence of chromium enables incandescent lighting to alter the color of a gem from bluish green in daylight to a warmer color such as pink, purple or red.

Chrome What?

Variety names for green gems such as 'chrome' diopside, 'chrome' chalcedony and 'chrome' demantoid are informative, as the primary cause of green color in these gems is correctly attributed to chromium. Unfortunately, the term 'chrome' is often used loosely in the trade to describe any bright green gem regardless of whether the primary coloring agent is chromium. This is partly due to marketing.

Placing the word 'chrome' in front of a gemstone name such as tourmaline adds considerable monetary value to the stone. The word 'chrome' is also used incorrectly in trade names due to general misconceptions about vanadium's role in green color. As a result, some gem varieties that are colored mostly by vanadium are referred to as 'chrome' gems.

'Chrome' tourmaline is a prime example. Chromium does contribute to the dark green color of 'chrome' tourmaline, and at times it can be the main coloring agent, but vanadium is most often the primary cause of color in 'chrome' tourmalines. A typical chrome tourmaline contains twice as much vanadium as chromium, and a more accurate trade name for this gem would be 'vanadium' tourmaline. As another example, all the dark green 'chrome' sphene gems that I have tested owe their color more to vanadium than to chromium.

The light green to dark green colors of 'chrome' kornerupine and 'chrome' Mali garnets are also due mostly to vanadium rather than to chromium. It's still common for the exquisite 'emerald' green color of tsavorite garnet to be mistakenly credited to chromium, even though research has shown that the average tsavorite garnet contains about 5 times more vanadium than chromium.

An unusual case of vanadium causing green color unexpectedly in a gem is a green 'chrome' chalcedony gem from Mexico that I purchased online.

Chromium is typically the main coloring agent found in chrome chalcedony, which is a green variety of microcrystalline quartz. Chrome chalcedony is found in a number of locations around the world, but Mexico is not a known origin.

I bought the unusual faceted gem as green chrysoprase (supposedly colored by nickel) from an online seller who prospected small rough specimens in Mexico and cut them himself. Tests I conducted in my lab show that the gem is not colored by nickel but instead by vanadium, along with a lesser amount of chromium. As far as I know, this is the first reported example of vanadium chalcedony, and the first known example of green chalcedony from Mexico.

Vanadium Chalcedony from Mexico

In Part Two, Kirk will look at ways to detect the presence chromium and vanadium using a Chelsea Filter, Dichroscope, UV Flashlight, Magnetic Wand, Blue Laser, Spectroscope and Spectrometer. He will also explore the causes of color in emerald and discuss the difference between emerald and green beryl.

All photographs by Kirk Feral

Australian Opal Centre

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