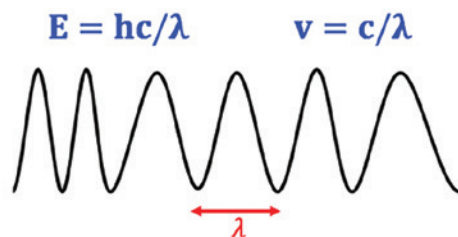


The Science of Ceramic Glaze Color

Written by Ryan Coppage

The colors we observe from surrounding objects are fascinating phenomena of their interaction with light. When a beam of light strikes an object, a portion of the light frequencies is absorbed by the object, whereas the unabsorbed wavelengths are reflected back to our eyes. The light receptors inside our eyes convey these *messages* to the brain, producing our perception of a color associated with the object.^{1,2} Light consists of a continuum of frequencies with corresponding wavelengths and energy levels. The relationship between energy and wavelength can be explained by the equation: $E=hc/\lambda$, in which λ is the wavelength value, E is the energy, c is the speed of light and h is Planck's constant.^{3,4,5} The frequency value is reciprocally proportional to wavelength through the equation $v=c/\lambda$. (Figure 1a). As frequency increases for an incidence of light, shorter wavelengths are present with greater energy (Figure 1b).



E : energy (Joules)
 h : Planck's constant (6.6×10^{-34} J/s)
 c : speed of light (3×10^8 m/s)
 λ : wavelength (m)
 v : frequency (1/s)

Figure 1a: The relationship between energy and wavelength.

390 420 445 485 520 558 587 610 660 710 780

Wavelength (in nm) and corresponding colors in the visible spectrum.

The Shorter the wavelength the greater the frequency is with a higher corresponding energy.

Figure 1b: The visible spectrum with wavelength values (in nm) and corresponding colors.

Human eyes are only able to process light and color within a certain range of wavelengths (400-700 nm), the visible spectrum region. The colors detectable by our eyes in this region are red, orange, yellow, green, blue, and violet (from the longest to shortest wavelength).⁶ Colorless and transparent objects absorb wavelengths outside of the visible region, thus their light reflection is not recognizable as any color by our eyes. Black objects are perceived as possessing an *absence of colors* by our brain because they absorb all of the wavelengths in this region and reflect nothing back.

An object's color absorbance and reflection properties are dictated by its molecular structure and composition.⁷ Atoms consist of a positively charged central core and a cloud of electrons which are negatively charged particles.⁸ Around the central core, electrons move in a region of space called orbitals, which possess different shapes and energy levels and are responsible for bonding between elements.^{8,9}

In transition metals, there are five d-orbitals that are normally equal in energy.⁹ When a metal is suspended in a crystal field (a gemstone, glaze, or otherwise,) parts of the surrounding environment start to interact with those orbitals. As they are more (or less) negative or move in closer (or are farther away), the surrounding environment starts to change the energy spacing of the orbitals.^{10,11}

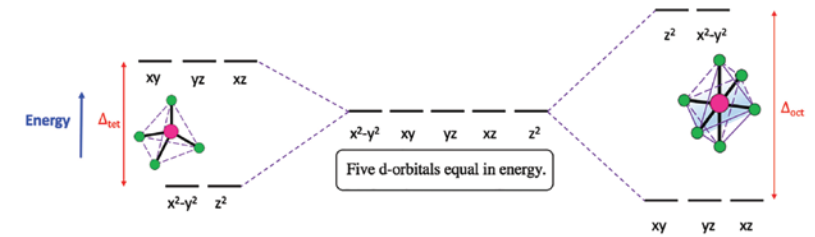


Figure 2: Splitting patterns in energy levels of d-orbitals with respect to the co-ordination geometries of the metal compound.

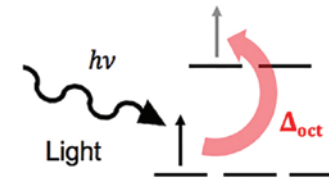


Figure 3: Light absorption stimulates electron promotion from lower to higher energy level.

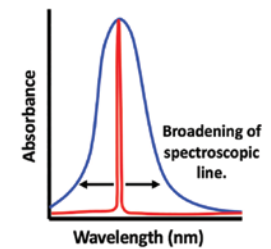


Figure 4: Broadening of the spectroscopic spectrum.

Different geometries of these interactions form a range of energy spacing patterns (Figure 2) – mostly tetrahedral and octahedral. During orbital interaction, the five d-orbitals are split into two different sets of energy, wherein a gap between energy levels can exist.¹¹

As light strikes an electron in a metal, it can be promoted from one of these lower energy levels to one of the higher ones, with the total energy of the promotion proportional to the wavelength (and color!) of the light absorbed (Figure 3).^{7,12} By inducing light of a specific range of wavelength on a substance's surface using a spectrophotometer, light absorption of a substance can be measured. The value of this measurement is called the absorbance and corresponds to a specific amount of energy required for the electron transition.¹³ Across a continuum of wavelengths and corresponding absorbances/reflections for a metal in a crystal field, spectroscopic information can be collected to create a reflectance spectra – the reflected and absorbed color profile of the metal in its environment. Though this is theoretically described as a single transition with a very absolute energy gap, this transition event is not as narrow and absolute as expected. There are several factors that contribute to the broadening of absorption events by transition metals. Through changes in vibrational and energy states of the particles and the interaction between these vibrations with the instrument itself, a single absorption even will take place across a range of wavelengths. The combination of these factors yield us a Voigt profile of the

spectroscopic spectra, allowing for a more broad color range instead of one particular wavelength of absorption (Figure 4).^{14,15}

The colors we perceive are those not absorbed by the metal color centers – the reflected wavelengths of light whose energies do not correspond to that energy gap – as all remaining light that wasn't absorbed. The energy of this gap depends on the transition metal, the charge of the transition metal, the electronic nature of the crystal field (glaze base) around it, and their arrangement around the metal center.¹⁶ Transition metals have distinctive light absorption and reflection properties. Varying the charge on a metal center or the crystal field surrounding it changes the electronic interaction between them, thus changing the energy gap between orbitals and the wavelengths of light absorbed (and reflected back).^{16,17}

The science of color is a common phenomenon in our everyday lives, from nearly every product available to the red corvette you watched speed around the corner. To that end, the pigment industry is projected to reach a net worth of 34.2 billion dollars by 2020.¹⁸ The constantly increasing demand in organic dyes and pigments reflects the growing desire of developing high performance color products that are environmentally friendly parallel to ever-increasing performance standards. A color market with a net worth in the billions of dollars warrants very specialized techniques and an incredible degree of understanding of the science of color.

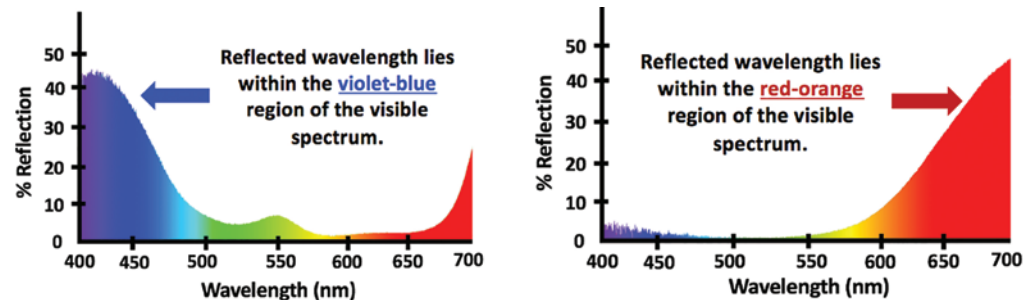


Figure 5: Reflectance colour profile of a) cobalt compound in glaze and b) chromium compound (with tin oxide) in glaze.

In mineralogy, the colors in gemstones can be explained by their material makeup and the identity of the transition metal impurity in them.¹⁹ The various colors in cuprite and malachite are explained by differences in oxidation states of copper ions in their crystal structures.²⁰ The presence of Cu+1 in cuprite yields a green light absorption, which corresponds to the gemstone's distinctive vibrant red color. Increasing the charge on copper from +1 in cuprite to +2 in copper carbonate yields a larger charge density and allows the ligands to be closer to a Cu+2 than to a Cu+1 ion center.^{21,22} The smaller distance between ligands and metal central ions causes a greater repulsion force between them during their interaction and creates a smaller energy gap, explaining the longer wavelength absorption in copper carbonate and the reflection of color green in malachite.^{21,22} Both rubies and sapphires contain corundum, also known as crystalline alumina, Al₂O₃; however, their colors are vastly different from each other. The blue color in sapphire is a result of the interaction between the alumina and ions of iron and titanium, whereas the red color of rubies is derived from trace amounts of chromium in the corundum structure.^{23,24} Similarly, the difference between emeralds and rubies is also very slight. Even though they both contain a chromium impurity for color, emeralds are constructed from beryllium aluminum silicate (beryl) as opposed to corundum. This difference in coordination environments around chromium affects the energy gap enough to shift the transmitted light, controlling whether the gemstone will be green as in emerald or red as in the case of ruby.²⁵

Crystal field theory via gemstone color makes for a nearly perfect model to explain the transition metal d-orbital splitting phenomena in ceramic glaze color. The silicate matrix in ceramic glazes is effectively a crystal coordination environment.²⁶ Without any additional ingredients or opacifiers, glaze layers would remain transparent and colorless, resembling a thin, glossy coating.

By selectively adding transition metals oxides, a variety of colors can be created to effectively produce a metal-based color rainbow.^{27,28} The presence of copper carbonate in glazes, similar to malachite, can generate a wide range of hues from aqua to green to a vibrant red depending on its concentration and oxidation state.²⁹ Emerald's distinctive green color in glaze can be recreated using chromium oxide. Cobalt can be used to generate a strong blue-violet (Figure 5a). Additionally, the crystal field around chromium can be altered with the addition of tin oxide, yielding a ruby red color in glazes (Figure 5b).³⁰

Light reflection properties (color) of transition metals can be characterized using several spectroscopic techniques.³¹ Through these techniques, we can quantitate the relationship between transition metal content in a glaze and its corresponding color, absorbance/reflectance bands, and the intensity of these events to build complex color profiles. This allows for the development of complex color quality and intensity, corresponding to the concentration and identity of the metal colorants. This approach could potentially allow for a library of color information and for the ability to design glaze color profiles without the time and material waste typically observed in traditional testing and formulation processes.

Glaze color and reflectance profiles

A series of glaze color measurements were carried out to evaluate the reflectance color profile of various transition metals in a clear glaze base. The instrument used in these experiments is a portable Ocean View FX spectrometer with scanning capacity from 300 to 1000 nm. Reflectance spectra corresponding to each colored glaze was collected in the 300-1000 nm wavelength range; however, the results produced within the visible region, 400-700 nm, are shown.

The following series of colored glazes, including cobalt carbonate, copper carbonate, manganese dioxide and iron oxide, was fired and characterized using Celadon base recipe (Figure 6).

Nepheline Syenite	56.3%
Gerstley Borate	12.5%
Calcium Carbonate	10.4%
Silicon Dioxide	20.8%

Figure 6: Celadon base recipe.

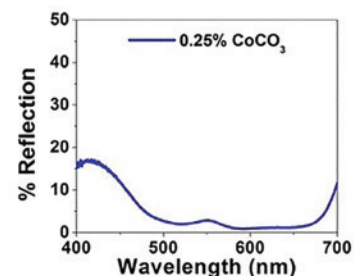


Figure 7: Color profile of cobalt carbonate.

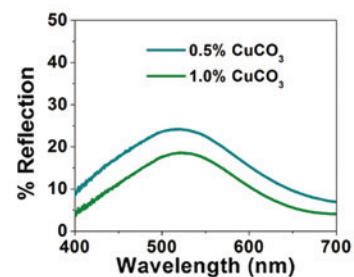
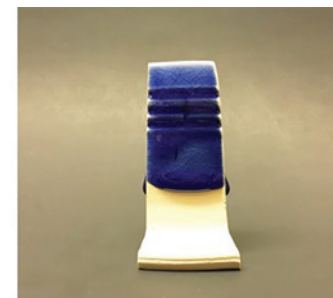


Figure 8: Color profile of copper carbonate. Samples show increasing concentration from left to right.

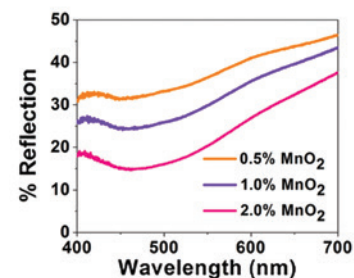


Figure 9: Color profile of manganese dioxide. Samples show increasing concentration from left to right.

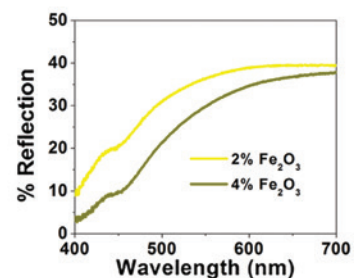
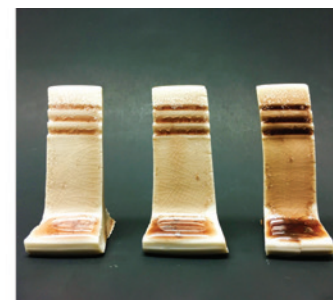
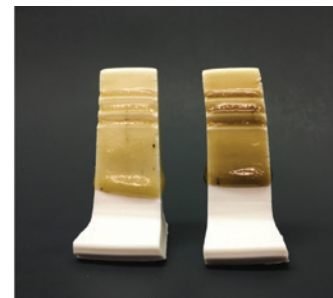


Figure 10: Color profile of iron oxide. Samples show increasing concentration from left to right.



Cobalt carbonate

The color profile of cobalt carbonate (Figure 7) shows that the reflectance spectral profile of cobalt carbonate in glaze exhibits higher magnitude light reflectance in the violet-blue region (400-450 nm). Even though there is another smaller peak in the blue-green region (550 nm) displayed in the spectral profile, the reflection intensity from the violet-blue region is much greater, which explains the glaze's distinct blue color. Additionally, there is a small red color present – perhaps adding a violet nature to the glaze. As expected, the transmission peak is visibly broadened and covers a wavelength range instead of being displayed into individual lines.

Copper carbonate

The reflectance profiles of copper carbonate (Figure 8) in glaze displays light reflectance in the blue-green and green-yellow region (475 - 560 nm). Their transmission peaks are also broadened and cover the entire visible spectrum with particularly greater magnitude in these regions, creating a very broad and deep green. Noticeably, the shapes of these peaks possess significance resemblance to one another. A larger quantity of copper (right sample) yields a lower reflection intensity in comparison with a smaller amount of copper (left sample), explaining the differences in their shades. This can be explained as a more defined, darker color, as less net light is reflected off of the sample, resulting in a lower % reflection value.

Manganese dioxide

It is not commonly known that trace amounts of manganese dioxide yields a mauve pink color in ceramic glazes (Figure 9), which matches the reflectance spectra of the tiles in the orange-red region (600-700 nm) with some minor light reflectance in the violet-blue region (400 nm). As the manganese dioxide content is increased, the combined reflectance profiles transition to presenting a brown color, and eventually a black, as manganese dioxide is a common additive for brown/black slips. The transmission peaks recorded in their spectra are extremely broadened, suggesting no simple, true color that is limited to just one region of the visible spectrum. The light reflectance in both violet and orange-red regions explains the dark orange color of the manganese dioxide at 2.0%, which would transition to a brown and eventually a black at higher percentages. Similar to the

copper samples, the shapes of the reflectance spectra of all three manganese samples are similar. From left to right, the color goes from the lightest to the darkest tint, corresponding to the lowest to the highest manganese content in glazes – as highest to lowest % reflection measurements.

Iron oxide

Ferric oxide (Red Iron Oxide, Fe₂O₃, RIO - Figure 10) can be employed as a greenish-yellow colorant in ceramic glazes, as a gold/tan color in amber celadons, as a crystallized tomato red iron, or as a surface-crystallized black glaze – as the Raku family used it hundreds of years ago on ceremonial chawan. Iron oxide's spectral profile displays a strong light reflectance in the teal to red region (550-700 nm). As expected, the transmission peaks recorded in their spectra are extremely broadened, covering a majority of the visible spectrum and transitioning into the infrared region. The shapes of these peaks are also of great resemblance to one another, even possessing the minor reflectance peak at 440 nm. The iron oxide loading (2% and 4%) and color relationship trend in both manganese and copper samples is also true in this case. The sample with a larger amount of iron oxide (right sample) establishes a lower reflection intensity compared to the one with a smaller content of Fe₂O₃ (left sample).

Copper carbonate (reduction and oxidation)

Mentioned previously, changes in charge on copper ions correspond to the color differences between malachite and cuprite gemstones. Similarly in glazes, changing the oxidation state of the metal center during reduction or oxidation firing can also affect the colors obtained from glazes with this metal (Figure 11). In copper carbonate, copper has the oxidation state of 2+, yielding deep green/teal colors in glazes. Under reduction firing, copper accepts one electron and the charge changes to 1+, resulting in an intense ruby red color. As expected, both transmission peaks in these two samples are somewhat broadened. The oxidation-fired copper sample displays a strong light reflectance in the blue-teal region (500 nm), which helps explain its green-blue color. Conversely, the reduction-fired copper sample produced light reflectance in the orange-red region (650-700 nm), which corresponds to its red color. These, much like chromium, contribute to the crystal field theory of metal color centers and paint a very informative picture of glaze color mechanism.

Even though they both contain a chromium impurity for color, emeralds are constructed from beryllium aluminum silicate (beryl) as opposed to corundum.

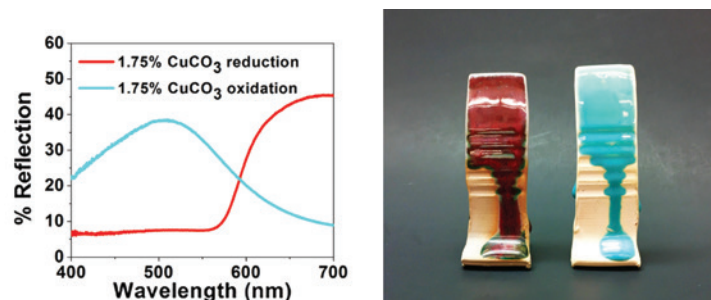


Figure 11: Color profile of copper carbonate. Reduction or oxidation firing results in different glaze color.

G. Borate	21%
Nepheline Syenite	16%
EPK	11%
Whiting	20%
Silica	32%

Figure 12: Chromium base recipe.

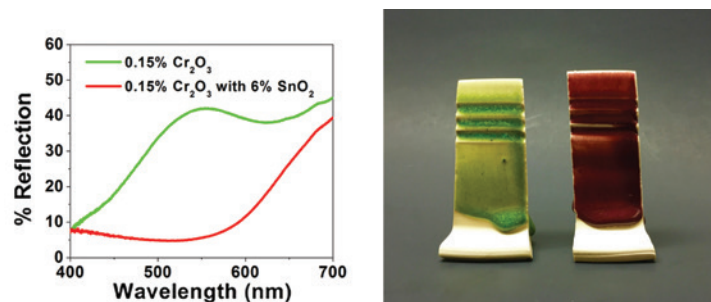


Figure 13: Color profile of chromium oxide. 0.15% Chromium Dioxide (left tile) produces an emerald green. The addition of tin dioxide changed the reflectance color to ruby red.

Chromium oxide

The chromium oxide ruby red and emerald green glazes (Figure 13) were fired and characterized using chromium recipe base (Figure 12).

As mentioned above, differences in coordination environments determine what the color of gemstones will be – green as in emerald or red as in the case of ruby for chromium. Using trace amounts of chromium oxide, these colors can be replicated in ceramic glazes. Without any

other additive, the emerald green color can be recreated in glaze using just 0.15% chromium oxide (tile, left). With the incorporation of tin oxide, the coordination environment around chromium is changed, yielding a ruby red color (tile, right). The resulted spectral profiles match their color description. A strong light reflectance in the green-yellow region (500-600 nm) is detected in the emerald green tile. For the ruby red tile, this peak disappears and a strong light reflectance peak in the red region (700 nm) is observed. The ruby red sample establishes one broadened singular peak in the red region that also stretches into the IR region, explaining the intensity of its color. On the other hand, the emerald green sample displays a broadened peak in the green-yellow region and another one in the orange-red region that also transitions into the infrared spectrum. This explains the subtle blend in its color profile between green and yellow and also provides some information about the ability to have red reflectance be a domination color.

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About the author

Ryan Coppage is drawn to the Venn overlap between science and art that is not often characterized or fully explored. From an art perspective, materials chemistry is a perfect platform from which to examine and explain color, surface texture, crazing, and desirable ceramic surface effects. He currently works on research projects that are frequently split between the University of Richmond and the Visual Arts Center of Richmond, developing low metal loading color alternatives for ceramic surfaces.

Summary

This series of glaze studies, color profiles, and reflectance measurements should allow for a better understanding of metal color behavior in ceramic glazes. Through understanding d-orbital splitting of transition metals, metal oxidation states through firing, crystal field nature of the glaze base, and the corresponding color profiles of these systems, glazes can be better designed in the future and with less waste during formulation/testing. To that end, incremental metal colorant loading in glazes could be used to determine color reflectance patterns to create a library of glaze and color information – allowing one to merely select the color and intensity they desire from a pallet, upon which a glaze recipe and metal colorant loading would could be calculated and provided. Additionally, these reflectance profiles can allow for a more manageable and time-saving characterization of color quality and intensity, corresponding to the loading, glaze base needed, and firing techniques required for each color. Ultimately, this represents the potential for a color information reference library without the consumption of thousands of hours testing or kilograms of materials wasted. ■

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