Axinite: Magnetism & Color

Overview

https://www.gemstonemagnetism.com/axinite

Axinite is an intriguing group of mineral species whose triclinic crystals form as thin blades with sharp edges reminiscent of axe blades, hence the name Axinite. Like Tourmaline, Axinite is a borosilicate mineral containing a significant amount of boron in its native chemistry, along with transition metals that often cause strong paramagnetism. Brown is the most common color in Axinite gems, but rare examples can have a surprising variety of colors including yellow, lavender, pink, blue, green, and orange. Axinite can also be completely colorless. Strong longwave UV fluorescence is a feature of some Axinite gems, while color zoning, pleochroism and color change can be found in all species of gem Axinite.

Axinite Crystals on Matrix, 25 mm Tall, Luning, Nevada

Axinite mineral specimens are less than ideal for fabricating into gems, as transparent uncut crystals tend to be quite thin, often less than 5 mm in depth. As a gemstone, Axinite is obscure and of interest mostly to collectors of rare or unusual gems. But in recent years, mining in Tanzania of pale Axinites with unusual colors has stimulated interest in this gem mineral.

Magnetic testing can be quite helpful in the identification of Axinite, and this article presents the complete findings of our study of magnetism in Axinite. Much of this information is new and not published elsewhere. Depending on the species, magnetic response and measured magnetic susceptibility in Axinite can vary widely, from very Weak (SI < 20) to a Pickup response (SI 1879). However, most Axinite gems show a Drag response and have high measured magnetic susceptibility much like Peridot, around SI 500-600 (note: SI values are succeeded by 10^{-6}).

We curated and analyzed 53 Axinites: 37 faceted gems and 16 individual uncut crystals, plus 2 parcels of homogeneous rough crystals. All but 2 samples were transparent. Most uncut crystals in our study had at least one naturally flat smooth surface suitable for measuring refractive index and magnetic susceptibility. All samples were tested for refractive index, magnetic susceptibility, magnetic response, thermal inertia (thermal conductivity), longwave and shortwave UV fluorescence, pleochroic colors, color change, absorption spectrum (using a UV-Vis-NIR spectrometer) and Chelsea filter reaction. Hydrostatic specific gravity was measured only for samples above 2 ct. in weight to ensure accuracy.

In addition, we tested 6 rare and near-colorless Axinite gems at a gem show for magnetic response only. The brown Axinite pictured below is rare for its large size, depth, and flawless clarity, and it is the largest faceted Axinite tested for this study.

Ferroaxinite 10.02 ct, 13 mm X 9 mm X 6 mm, Pakistan

SI 608, Too Heavy to Drag

There are four species of Axinite, but only three of these are considered gem-quality. In gemology, the 3 gem Axinite species are usually referred to as Ferroaxinite (iron Axinite), Manganaxinite (manganese Axinite) and Magnesioaxinite (magnesium Axinite). In 2008 the International Mineralogy Association (IMA) officially re-named these three mineral species as Axinite-Fe, Axinite-Mn, and Axinite-Mg. The fourth species in the Axinite group is Tinzenite, a rare species typically found as clusters of small yellow or orange crystals colored by manganese.

Axinite gems found in the marketplace are mostly brown or yellowish-brown Ferroaxinites and Manganaxinites. A curious aspect of brown Axinites such as the 4 mm-deep rough crystal pictured below is that they can appear dark brown in reflected light, but near-colorless in transmitted light. Rotation of this crystal reveals that this change from dark to light color may be due to light extinction that varies with the orientation or angle of the stone under reflected light. The intensity of brown color also varies throughout the crystal. Due to high iron content, the crystal below has the highest measured magnetic susceptibility (SI 654) of any Ferroaxinite we tested.

Reflected Light *Transmitted Light*

Ferroaxinite Crystal, 12.72ct., 20 mm Tall, Pakistan, SI 654, Drag

Core to rim chemical zoning is known to be common in Axinite crystals. In Ferroaxinite, concentrations of iron tend to be higher near the core, and manganese concentrations higher at the rim. A single crystal can potentially contain the chemistry of two different Axinite species. However, we did not detect chemical zoning in our samples, as most rough crystals were measured for magnetic susceptibility at only one crystal face.

The refractive index for Axinite ranges from a low of RI 1.656 in Magnesioaxinite to a high of RI 1.704 in Tinzenite. We find that most Axinite gems fall within the range of RI 1.660-1.686. Our specific gravity measurements ranged from SG 3.14 in Magnesioaxinite to 3.38 in Tinzenite, with typical Axinites ranging from SG 3.24-3.32. We did not find specific gravity measurements to be consistently proportional to magnetic susceptibility.

Axinite is found in many locations around the world, but today the majority of faceted Ferroaxinite and Manganaxinite gems are supplied by Pakistan, with France being noteworthy secondary source. Magnesioaxinite is the rarest species of gem Axinite, and cut gems are very rare. Light-colored Magnesioaxinites, as well as light-colored Manganaxinites, originate primarily from Tanzania. They are mined in Merelani Hills, Tanzania within the same mines as Tanzanite and Tsavorite Garnet. Additional geographical sources of Axinite samples examined in our study include Afghanistan, Russia, Sri Lanka, Brazil, Italy, and Nevada (U.S.A).

Understanding Axinite through Magnetism

Axinite gems are well suited to study and identification via magnetic testing due to two transition metals inherent in their chemistry: iron and manganese, the same magnetic metals that allow us to analyze Garnet composition in detail and identify Garnets by species and variety (see A Graph of All Gem Garnets (gemstonemagnetism.com). The metal oxides of iron (FeO) and manganese (MnO) found within Axinite are both highly paramagnetic. Iron oxide (FeO) with 2 unpaired electrons (Fe^{2+}) creates brown color in Axinite, and manganese oxide (MnO) with 2 unpaired electrons (Mn^{2+}) is associated with yellow and orange color.

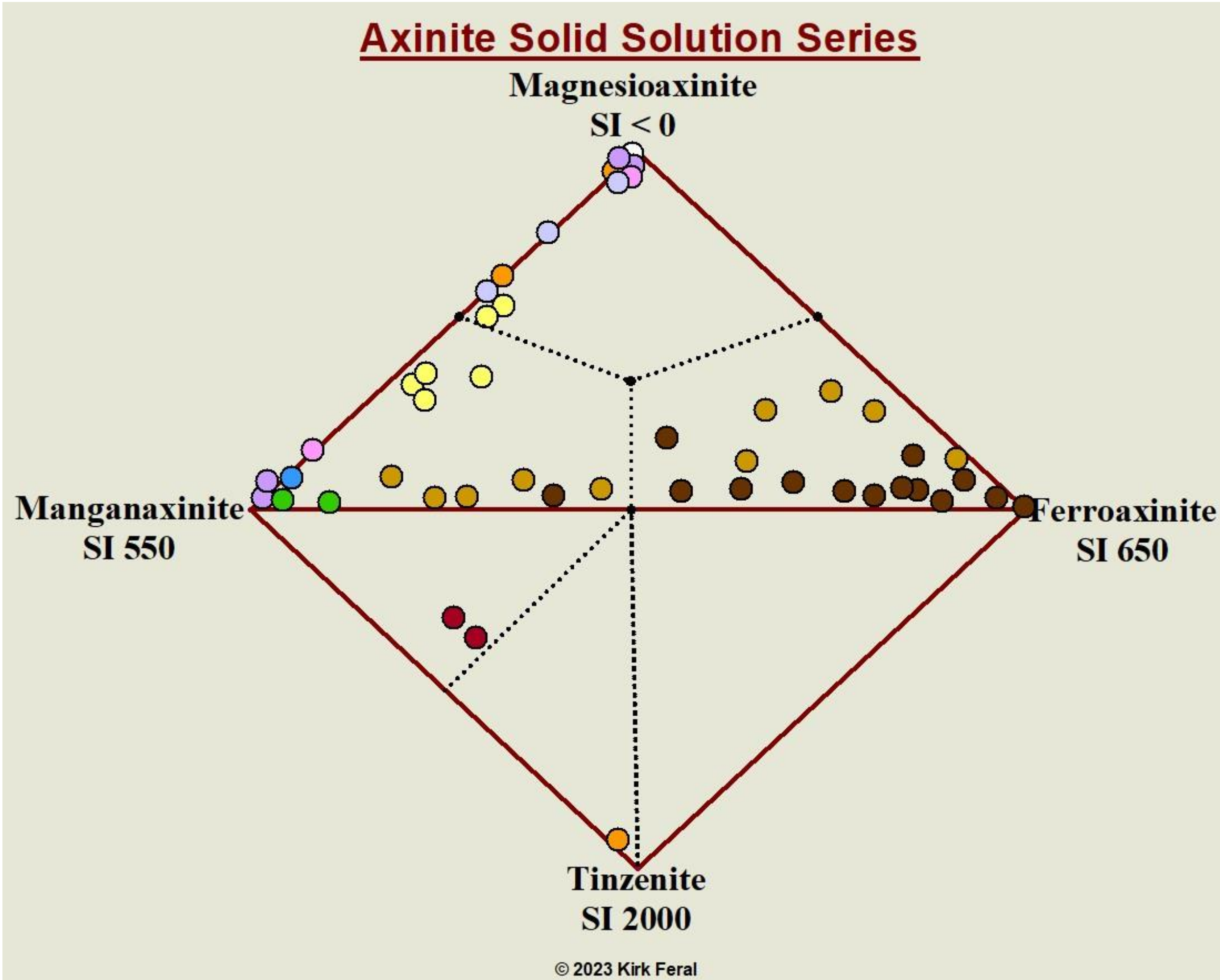
The third critical metal found in Axinite's chemical makeup is magnesium, which is not a transition metal and not paramagnetic. Magnesium oxide (MgO) is diamagnetic and produces no color. Since magnesium does not cause magnetic attraction, a simple magnetic test allows us to distinguish Magnesioaxinite from Manganaxinite (Williams, B. & C., 2014) and from Ferroaxinite.

A key finding of our study is that the common misidentification of Magnesioaxinite can be solved with a simple magnetic test. As a rule, Ferroaxinite and Manganaxinite gems of average size and weight (0.5ct – 6ct) show a Drag response to a ½" N52 neodymium magnet, while most Magnesioaxinite gems and crystals do not show a direct response and instead require floatation for any magnetic response to be visible.

Ferroaxinite 1.29ct, Brazil

SI 608, Drag

As with many other mineral groups such as Garnet, Tourmaline, and Spinel, the different species within the Axinite group chemically mix with each other in solid solution series, resulting in a range of colors and magnetic susceptibilities. The quaternary diagram drafted for this study (shown below) illustrates how the Axinite samples we tested intermix among the 4 species of Axinite.



Axinite Species Mix with Each Other in Solid Solution Series

In the above diagram, the 4 endmember Axinite species are labeled at the 4 corners of the quaternary. An estimated magnetic susceptibility value (SI) for the pure species endmember is listed under each species name based on the maximum SI value that we measured among samples we tested.

Mineralogists have measured actual magnetic mass susceptibility values for pure Axinite endmembers using a SQUID magnetometer (Filip, J. et al., 2008). However, the values that we use in the study of gemstone paramagnetism - magnetic susceptibility per unit volume in terms of SI X 10^{-6} - have not been determined for pure Axinite endmembers. The exception is Magnesioaxinite, which we know must have a value less than zero (SI < 0) due to the diamagnetic nature of magnesium oxide.

The diagram above shows the location of colored points at varying distances from endmember species, illustrating approximate compositions of the Axinites tested in this study. The colors of the points roughly correspond to the actual colors of the Axinite samples. The dotted lines represent the compositional boundaries between the Axinites species.

Orange-Brown Manganaxinite, 1.5ct, Pakistan

SI 525, Drag

Because any Axinite gem can be a blend of 3 species in varying proportions, accurate identification of the primary species content often requires advanced testing beyond the scope of this study. But standard gem identification tests along with magnetic susceptibility measurements, gem color and other criteria can be quite useful for identifying species and approximating the degree of mixing between species.

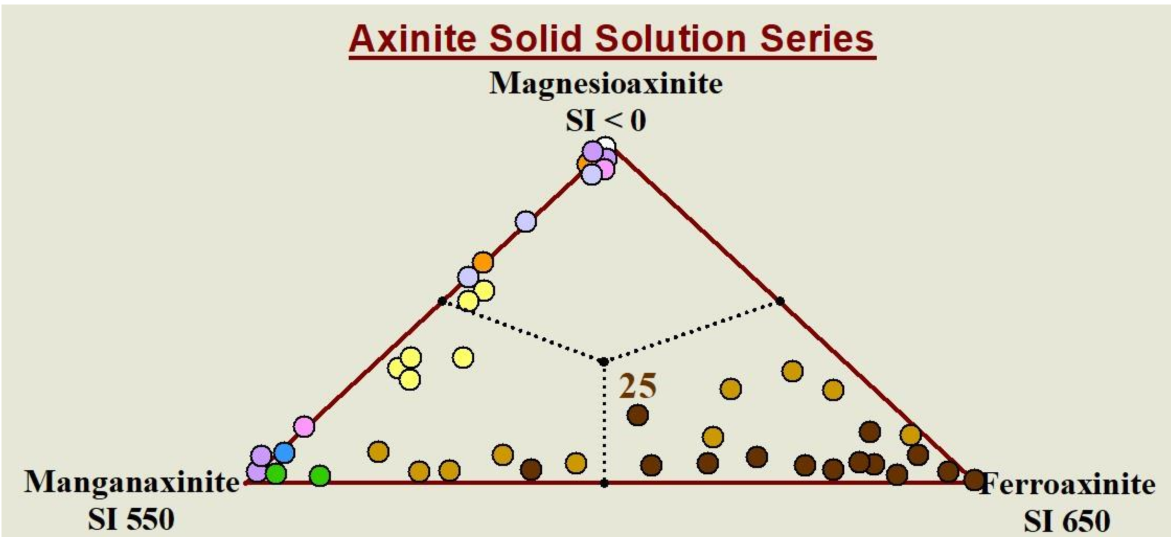
Point positioning in the above 2-dimensional diagram is based primarily on the single vertical axis variable of magnetic susceptibility, and no horizontal axis variable such as refractive index or specific gravity was assigned. We have high confidence in the approximate positioning of points located near endmembers and also the vertical poisoning of points that show the degree of mixing with Magnesioaxinite in the upper ternary, and with Tinzenite in the lower ternary.

Horizontal point positions along the line joining Ferroaxinite and Manganaxinite are the least accurate and represent our best guesses as to the proportion of iron to manganese within each Axinite sample based on absorption spectra, color, color intensity, and relative magnetic susceptibility.

As an example, we conclude that the composition of the gem pictured below is predominantly Ferroaxinite (brown color) with a considerable amount of Manganaxinite (yellow color), and we position its point (# **25** on the diagram below) just to the right of the boundary separating those 2 species. The relatively low magnetic susceptibility (SI 418) of this gem indicates that it also contains a significant amount of Magnesioaxinite, which raises the position of the point vertically toward Magnesioaxinite. Therefor the composition of Ferroaxinite gem # 25 is a mix of all 3 species of gem Axinite.

Ferroaxinite # 25, 0.72ct, Pakistan

SI 418, Drag



Ferroaxinite # 25 Mixes with Manganaxinite & Magnesioaxinite

An important new and unexpected finding of our study is that there is no miscibility gap between Magnesioaxinite and Manganaxinite among the samples we tested. Multiple samples of Axinite were found to have intermediate composition between Magnesoaxinite and Manganaxinite, especially within the Magnesioaxinite species. This finding is at odds with several studies of Axinite composition which performed electron microprobe analysis of Axinite samples. Those studies suggested that there is a miscibility gap or barrier between Magnesioaxinite and Manganaxinite, with minimal intermixing between the two species. They found that most samples of Magnesioaxinite were near the pure endmember in composition (Pringle & Kawachi, 1980; Andreozzi, G. et al., 2000). However, using magnetic susceptibility as an indicator of miscibility (i.e. mixing), we were surprised to find no such miscibility gap among our samples. The discrepancy between research results could be due to inequalities among samples tested.

Separating Axinite by Species

Gem color alone is not a reliable indicator for identifying Axinite by species. Nonetheless, a complete absence of brown color rules out Ferroaxinite. Bivalent iron (Fe^{2+}) is a strong coloring agent in Axinite, and even small amounts of iron can generate brown color. Brown Axinite gems are generally sold as Ferroaxinites, but our analyses show that some of these brown gems are likely Manganaxinites. Brown color has also been reported in iron-rich Magnesioaxinite gems from Pakistan (Zwaan J.C. et al., 2018), and a few brown Magnesioaxinite specimens have been found in other locations globally (Lauf, R., 2007), but we did not find any brown Magnesioaxinites in our study.

Ferroaxinite Crystal, 6.8ct

SI 573, Drag

Refractive index and specific gravity are not particularly effective for separating Axinite gems by species, as readings can show considerable overlap. However, Magneisoaxinite has the lowest RI and SG ranges, and Magnesioaxinites that are near the pure endmember can be separated from other Axinite species solely by their low refractive index (RI 1.656 - 1.678) and low specific gravity (SG 3.14 - 3.17).

When gems have brown body color, distinguishing between Ferroaxinite and Manganaxinite can be challenging without definitive data about chemical composition obtained from electron-microprobe analysis, EDXRF (energy dispersive Xray diffraction), SEM (scanning electron microscope) or other specialized testing methods. We find that Manganaxinites close to endmember composition have a higher refractive index than Ferroaxinites, but due to extensive intermixing between species, RI readings are generally not helpful in separating these two species when the have similar color.

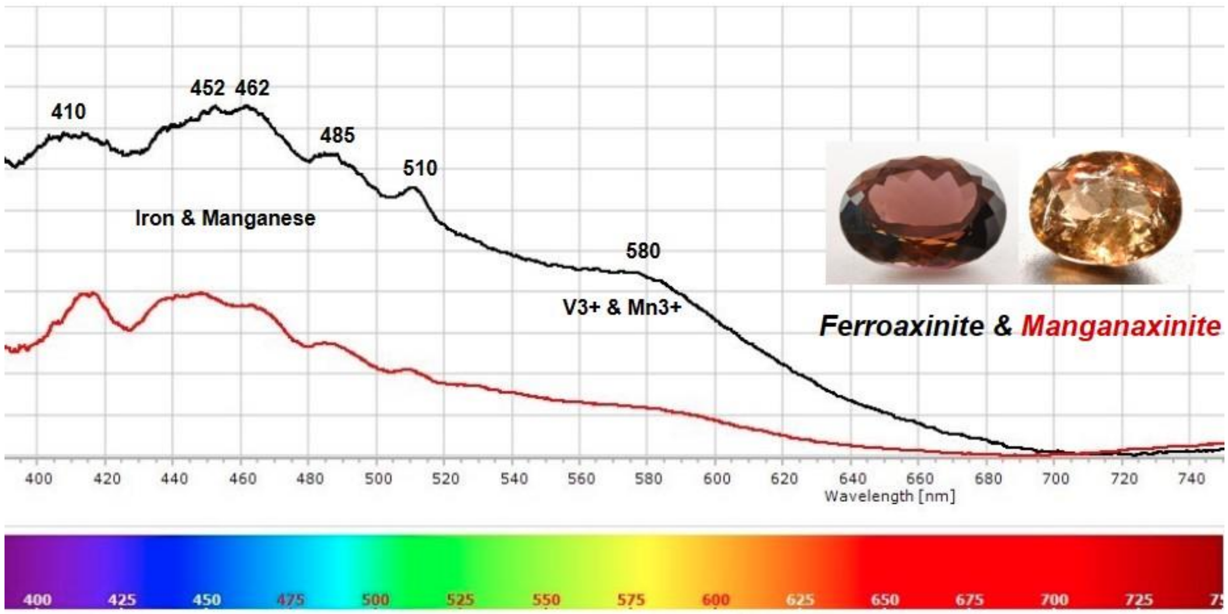
Brownish Yellow Manganaxinite 6.15ct

SI 352, Too Heavy to Drag

Magnetic susceptibility measurements for Ferroaxinite and Manganaxinite also overlap, although we find that Ferroaxinite gems on average have magnetic susceptibility values that are about 10% higher than Manganaxinite gems. We cannot distinguish between iron and manganese with a magnet, and gems of both species typically show a Drag response to a magnetic wand.

UV-Vis-NIR spectrometer readings for brown Ferroaxinite and brownish yellow Manganaxinte gems also appear very similar since they both contain absorption features for iron and manganese. In the visible absorption spectrum graph shown below, we see that both the brown Ferroaxinite and yellow Manganaxinite absorb light in the blue and violet regions of the spectrum, represented by multiple small peaks from iron and manganese on the left side of the graph. On the right side of the graph, light transmission occurs in the green and red regions, which together result in brown color. Red + green = brown.

A broad absorption peak near 580nm at the yellow center of the graph is typical of the Ferroaxinites we examined. This peak represents yellow light absorption by vanadium and Mn3+. In contrast, this absorption peak at 580nm is mostly absent from Manganaxinite, and more yellow light is transmitted. We found that this minor difference in absorption spectra can be quite useful for distinguishing Manganaxinites from Ferroaxinites that have similar color.



Visible Absorption Spectra for Brown ***Ferroaxinite*** *& Yellow* ***Manganaxinite***

As the above spectra demonstrate, we can use color as one criterion for separating Axinite species, as increasing yellow color suggests greater manganese (Mn2+) content due to greater mixing with Manganaxinite. UV fluorescence indicates a lack of iron (Fe2+) content derived from Ferroaxinite. Lower magnetic susceptibility and lower color intensity are signs of mixing with Magnesioaxinte and/or Manganaxinite. The yellow Manganaxinite pictured below has a high magnetic susceptibility typical for Manganaxinite, but this gem does not fluoresce due to iron (brown color) from Ferroaxinite.

Brownish Yellow Manganaxinite, 1.1ct., Pakistan

SI 555, Drag

Light-colored Axinites that have no brown color can easily be separated by species using magnetic testing. If the gem or crystal is 0.5 - 6 ct. in weight, a Drag response to a magnetic wand informs us that the Axinite must be Manganaxinite, or very close to Manganaxinite in composition. (note: to test for a Drag response of a thin uncut Axinite crystal blade of any size or weight, the broad side of the crystal must rest against the pole of the magnetic wand).

An absence of any direct magnetic response indicates the Axinite is Magnesioaxinite, and floatation is necessary for any magnetic response to be visible. Depending on the amount of Manganaxinite in its composition, a Magnesioaxinite will show a magnetic response ranging from very Weak to Strong when floated. The crystal pictured below is near the pure Magnesioaxinite endmember in composition and has a very weak magnetic response when floated.

Lilac Magnesioaxinite, 10.35ct, 17 mm Tall, Tanzania

SI < 20, Weak

With the additional help of a Hoover magnetic susceptibility balance, magnetic measurements permit us to more precisely estimate the degree to which Magnesioaxinite intermixes with Manganaxinite or Ferroaxinite, and vice versa. The crystal above has a measured magnetic susceptibility of only SI < 20, confirming that it approaches pure endmember composition and does not mix with other Axinite species to any significant degree.

Ferroaxinite

The chemical formula for Ferroaxinite - $Ca_2\mathbf{Fe^{2+}}Al_2BSi_4O_{15}OH$ – specifies that iron (**Fe2+**) is the defining transition metal. Ferroaxinite was the first species of Axinite to be discovered. When the new mineral name Axinite was first adopted in 1797, other species in the mineral group were not known. The species name Ferroaxinite was not declared until 1909. Ferroaxinite is an idiochromatic (self-colored) species, colored primarily by bivalent iron (Fe2+) that produces brown color.

Color can be modified somewhat by the presence of additional coloring agents such as manganese (Mn2+ and Mn3+) and vanadium (V3+), resulting in yellowish brown, pinkish brown, and purplish brown body colors. Using a dichroscope, two or three colors (pleochroism) can often be seen in Ferroaxinite, and pleochroic colors can include yellow, pink, brownish purple, and sometimes green.

Pinkish Brown Ferroaxinite 3.2ct, Pakistan

SI 599, Drag

Color zoning is the unequal distribution of color, either body color or a secondary color. Secondary colors do occur in the Ferroaxinite species, although they are uncommon and can be obscured by dark brown color. Unlike pleochroism, where different colors are visible when the gem is viewed at different angles, color zoning occurs as discrete patches or streaks of color within the body of the gem. Below is an example of blue color zoning in dark brown Ferroaxinite, as it appears in transmitted light. The blue color is the result of vanadium irregularly distributed at the end of a 2 mm thin Ferroaxinite crystal from Pakistan.

Blue Color Zoning in Ferroaxinite

The 1.05ct brown Ferroaxinite cushion shown below has dark brown color and high magnetic susceptibility (SI 618). Although Ferroaxinite is not considered a color change species, we find that a noticeable color change under incandescent light toward brownish pink, brownish red or brownish orange is apparent in most Ferroaxinite gems and crystals. The pink/orange color in incandescent light may be related to the presence of trivalent manganese (Mn^{3+}), which can be present in Ferroaxinite (Chalmin, E. et al., 2008).

Ferroaxinite in Daylight & Incandescent Light

1.05ct, SI 618, Drag

Because iron quenches UV fluorescence, all Ferroaxinites are inert to UV light. Since iron oxide (FeO) is highly paramagnetic, Ferroaxinite gems typically show a Drag response to an N52 neodymium magnet and have the highest magnetic susceptibilities among the three gem Axinite species. Based on our magnetic susceptibility measurements, we estimate the potential range of susceptibility for the species to be SI 325-650, with measurements averaging around SI 600.

Ferroaxinite can blend with Magnesioaxinite, and as magnesium replaces iron (Fe^{2+}), the magnetic susceptibility decreases, and color intensity can become lighter. Intensity of brown color therefore may be at least somewhat related to the concentration of Fe^{2+}.

The crystal shown below left has the lightest color of any brown Axinite in our study and correspondingly has the lowest measured susceptibility of only SI 360. This appears to be an example of Ferroaxinite with lower iron (Fe^{2+}) content replaced by a significant amount of magnesium from Magnesioaxinite. The crystal is part of a parcel of 28 light brown Axinite roughs from Pakistan, all with similar low magnetic susceptibility.

Light Brown Ferroaxinite, 3.45ct, Pakistan

SI 360, Drag

Parcel of Light Brown Ferroaxinite

We were also able to test an anomalous example of a Ferroaxinite from Russia with black body color. In daylight, the faceted gem shown below appears black and opaque. Under magnification the gem is translucent at the facet edges. The black body color and opacity are due to a dense suspension of fine particle inclusions. This unusual Axinite gem shows color change from black in daylight to olive green in cool LED light.

Black Axinite in Daylight (lft) & Cool LED Light (rt), 2.13ct, Russia

SI 999, Pickup

Black Axinite from the same source as the gem above have been analyzed by Raman spectroscopy, and results were published in the *Journal of Gemmolgy* (Laurs, B., 2016). The inclusions were identified as Clinochlore, which is a greenish mineral that can have high iron content due to mixing with idiochromatic Chamosite.

Our magnetic measurements are consistent with unusually high iron content. The magnetic susceptibility of the black Axinite in our study is remarkably high at SI 998, while typical brown Ferroaxinite is near SI 600. It should be noted that faceted gemstones of any kind that contain magnetic inclusions that affect magnetic response or magnetic susceptibility measurements are rare.

Manganaxinite

Manganaxinite - $Ca_2\mathbf{Mn^{2+}}Al_2BSi_4O_{15}(OH)$ – is a manganese-rich form of Axinite that was first recognized in 1891 and officially named in 1909. Manganaxinite is an idiochromatic species that mixes freely with Ferroaxinite in a continuous solid solution series. Magnetic responses for Manganaxinite are the same as Ferroaxinite, with gems of both species showing a Drag response when of average weight.

Based on multiple measurements, we estimate the full range of magnetic susceptibility for Manganaxinite is SI 300-550, with most samples testing near the pure endmember at around SI 550, which is 15% lower than our estimate for the Ferroaxinite endmember (SI 650). Some brown Manganaxinites have a significant amount of iron (Fe+) from blending with Ferroaxinite, and such Manganaxinites can be indistinguishable in appearance from Ferroaxinites.

As an example, the Axinite gem pictured below has a mixture of brown and yellow color. Its refractive index RI 1.67-1.68 is typical for both Ferroaxinite and Manganaxinite. Its magnetic susceptibility (SI 545) is low for Ferroaxinite but typical for Manganaxinite. Since the color intensity is strong and undiluted, we don't ascribe the lower SI to mixing with Magnesioaxinite. The absorption spectrum for this gem also lacks the peak at 580nm typical of Ferroaxinite. We conclude this gem is composed primarily of Manganaxinite (yellow color) mixed with Ferroaxinite (brown color).

Yellowish Brown Manganaxinite, .55ct, Pakistan

SI 545, Drag

Like Ferroaxinite, Manganaxinite is not regarded as a color change species, but limited color change from yellowish brown color in daylight to brownish orange in incandescent light can be seen in some Manganaxinites. One unusual orangey brown sample from Brazil (pictured below) showed pronounced color change to bright orange in incandescent light. The orange color is presumably due to manganese.

Unusual Color Change in Manganaxinite, 1.4ct, Brazil

SI 562, Drag

Golden yellow and brownish yellow body color in Manganaxinite gems is uncommon, and color is no doubt the result of a combination of Mn^{2+} (yellow) along with a small amount of Fe^{2+} (brown). These light-colored yellow gems show no color change from daylight to incandescent light, and they also fail to fluoresce due to the presence of iron. All the yellow Axinite gems we tested were light in color and had significantly lower magnetic susceptibility (near SI 350) than other Manganaxinites, indicating lower manganese content and higher magnesium content from Magnesioaxinite. We did not find any yellow Manganaxinites that were near the Manganaxinite endmember in composition.

Yellow Manganaxinite 1.24ct, France

SI 347, Drag

Yellow Manganaxinite 4.65ct, France

SI 352, Drag

In Manganaxinites that approach pure endmember composition, iron (Fe^{2+}) is mostly absent, and we find examples where brown and yellow color are completely absent. Other colors produced by trace amounts of transition metals then become more discernable or dominant in Manganaxinite. A depletion of iron (Fe^{2+}) also permits UV fluorescence, a distinguishing feature of Manganaxinites that approach pure endmember composition.

Some Manganaxinite gems are pale in color because bivalent manganese (Mn^{2+}) is a weak coloring agent and may produce little or no color even when the concentration of

Mn^{2+} is high (up to 10% MnO by weight). This is also the case in Pyrope-Spessartine Garnet.

Another weak coloring agent that may fail to produce color in Axinite is trivalent iron (Fe^{3+}). We know this is the case in Grossular and Andradite Garnet. In Axinite, chemical research has shown that as the concentration of Mn^{2+} increases, so does the ratio of trivalent iron (Fe^{3+}) to bivalent iron (Fe^{2+}) (Andreozzi, G., 2000). The small amount of iron that remains in Manganaxinites near the pure endmember is mostly trivalent iron (Fe^{3+}). Hence most or all the color in endmember Manganaxinites can be the result of transition metals other than Mn^{2+}, Fe^{2+} or Fe^{3+}.

In contrast to bivalent manganese (Mn^{2+}), trivalent manganese (Mn^{3+}) is a very strong chromophore. Just a trace amount of trivalent manganese (Mn^{3+}) can create pink color (Vigier & Fritsch, 2020), and extremely low concentrations of vanadium (V^{3+}) can produce blue color in Axinite (Arlabosse, J. et al., 2008), A combination of vanadium and Mn^{3+} in trace amounts likely causes the pale lavender color seen in Manganaxinite gems such as the octagon pictured below. Fine examples of lavender Axinite gems like this are very rare in today's marketplace and nearly impossible to find.

Lavender Manganaxinite 2.9ct, Tanzania

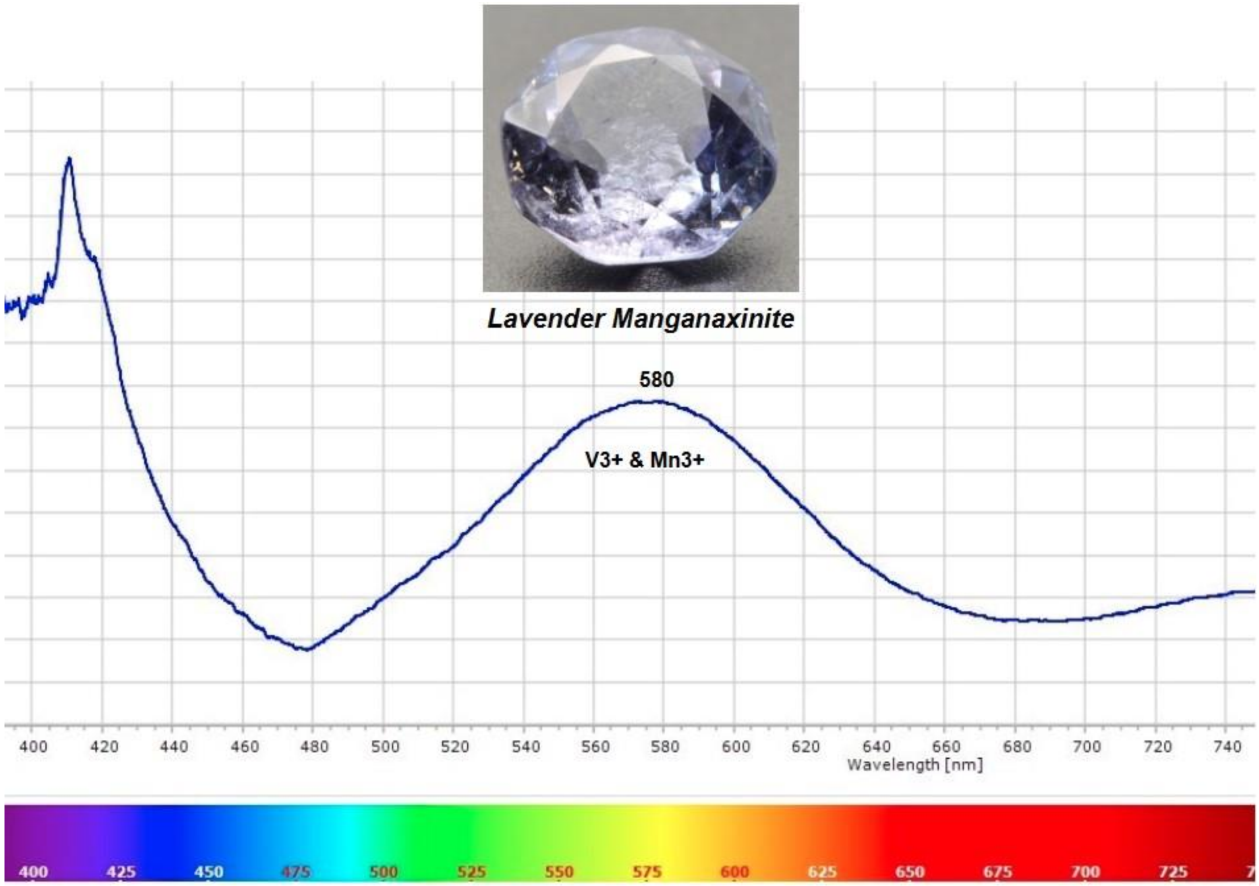
Daylight, SI 525, Drag

Because the gem above has no brown color (i.e. no Fe^{2+}) and at the same time has a high magnetic susceptibility (SI 525), we can infer that magnetism is due almost entirely to Mn^{2+}, and that chemical composition may approach the pure endmember for Manganaxinite. This gem also shows definitive color change from lavender in daylight to pink in incandescent light, presumably due to the presence of trivalent manganese (Mn^{3+}).

Lavender Manganaxinite Shows

Color Change in Incandescent Light

Lavender and pink Axinite gems show optical absorption spectra features that are different from brown and yellow Axinites whose color is controlled by iron (Fe^{2+}) and manganese (Mn^{2+}). The absorption spectrum illustrated below shows green and yellow light is absorbed at the broad peak in the center of the visible spectrum near 580nm. This light absorption can be attributed to a combination of vanadium (V^{3+}) and trivalent manganese (Mn^{3+}). Light transmission in the blue region occurs at the “valley” or transmission window on the left near 480nm, and red/pink color transmission takes place at the transmission window on the right near 680nm. Pale blue + pale pink = pale lavender.



Visible Absorption Spectrum for Lavender Manganaxinite

When longwave UV light is applied to this lavender octagon Manganaxinite gem, strong reddish orange fluorescence occurs, as pictured below. Orange fluorescence also occurs under shortwave UV light, but it is much weaker. The color of fluorescence in Axinite is believed to be the result of orange luminescence activated by manganese (Mn^{2+}) in combination with red luminescence activated by traces of chromium (Cr^{3+}) (Vigier & Fritsch, 2020). Similar pinkish orange fluorescence from manganese (Mn^{2+}) and chromium (Cr^{3+}) occurs in light-colored Grossular Garnets such as pale orange, pale green and colorless Grossular Garnets.

Lavender Manganaxinite Fluoresces Orange

Fluorescence in any type of gem or mineral is possible only when the concentration of iron is very low. The concentration of vanadium must also be very low, as vanadium can quench fluorescence as effectively as iron (Feral, K., 2019). While iron ($Fe2+$) and vanadium ($V3+$) both inhibit fluorescence when concentrations exceed trace amounts, manganese ($Mn2+$) activates fluorescence in Axinite.

While collecting our Axinite samples, we found frequent misidentification of light-colored Axinites such as the pale lavender gem shown above. Pale lavender Axinites from Tanzania are generally assumed to be Magnesioaxinites. Of the 7 lavender Axinites from Tanzania that we tested, all had been labelled as Magnesioaxinite, but all turned out to be Manganaxinite instead, showing a Drag response to our magnetic wand. Two of those lavender Axinites were mispresented in a 2017 issue of *Gems and Gemology* as Magnesioaxinite (Pay, D., 2017).

Lavender, lilac, or pale blue colors are indeed found in some Magnesioaxinites (Jang-Green, H. et al., 2007), but testing is of course necessary to verify the correct species. As we have shown, magnetic testing provides a simple way to separate light-colored Magnesioaxinte gems from Manganaxinite. If the Axinite is of average size and fails to show a direct response to a magnetic wand, the gem is Magnesioaxinite.

Pictured below is an unusual bicolor Manganaxinite crystal with natural internal fracture lines along the center. Pale brown color is apparent on the left side of the fracture and lavender color on the right. Although the brown color indicates the presence of iron ($Fe2+$), and pure lavender color signals the depletion of iron ($Fe2+$), the measured magnetic susceptibility on both sides of this large crystal is identical. Orange UV fluorescence on both sides is also equally strong, suggesting that the concentration of $Fe2+$ on the left side is too low (< 0.1 wt% FeO) to inhibit fluorescence or affect magnetic susceptibility even though it is sufficient to create very pale brown color.

Bicolor Manganaxinite, 18ct, 18 mm Wide, Tanzania, Strong UV Fluorescence Throughout, SI 556, Too Heavy to Drag

In the mines of Tanzania, lavender Manganaxinite can be found along with Tanzanite (purple Zoisite), and such Axinite crystals have been mistaken for pale Tanzanite. Both minerals are pleochroic, and the refractive index of Tanzanite (RI 1.69-1.70) is only a bit higher than that of Manganaxinite (RI 1.67-1.68). But it’s a simple matter to distinguish between these two minerals with a magnetic wand.

The small Manganaxinite gem shown below left shows a Pickup response due to its light weight (0.18ct). The Tanzanite shown below right is magnetically Inert (Diamagnetic), as we would expect of any transparent Zoisite. Another easy way to separate these look-alike gems is to check for longwave UV fluorescence. Lavender Manganaxinite shows strong orange fluorescence, and Tanzanite is inert to UV light.

Lavender Manganaxinite .18ct Tanzania   *Lavender Tanzanite .87ct Tanzania*

Pink color, with no blue color component from vanadium, occurs in Axinite, although pink color has only been reported in the Magnesioaxinte species. Pictured below, we present what we believe is the first reported and documented example of pink Manganaxinite. This pale pink crystal appears identical in color to pale pink Magnesioaxinites that we have tested, but the high magnetic susceptibility (SI 477) of this crystal clearly distinguishes it as Manganaxinite. The crystal also shows strong LWUV orange fluorescence and has a specific gravity of 3.22.

Pink Manganaxinite, 5.27ct, 16 mm Tall

SI 477, Drag

Color zoning can be found in all 3 species of gem Axinite, but perhaps the most striking examples are seen in Manganaxinite gems. Since Manganaxinite can be light in color, instances of color zoning stand out more clearly than in Ferroaxinite. The rarest colors found in Axinite are blue and green. Blue color zoning is due to traces of vanadium that are unevenly incorporated into the crystal. The Manganaxinite gem shown below has areas of dark blue color within a transparent light gray body.

Blue Zoning in Manganaxinite 1.05ct, Pakistan

SI 543, Drag

Green color may be the rarest color found in Axinite. Although the cause of green color has not been specified or documented in published literature, we suspect a trace amount of chromium (Cr^{3+}) might be the source of color, as chromium frequently produces green color in gems and is a known trace element in Axinite. The light-colored brownish-yellow Manganaxinite gem pictured below has green color zoning. This gem was incorrectly sold as Magnesioaxinite, presumably because of its light body color.

Green Zoning in Manganaxinite .6 ct, Pakistan

SI 545, Drag

The remarkable oval Axinite gem pictured below contains zones of blue and green color cohabiting the same stone. This gem has a near-colorless yellow-gray body and was also incorrectly sold as Magnesioaxinite, but a Drag magnetic response immediately rules out Magnesioaxinite. The light body color in conjunction with high magnetic susceptibility (SI 564) informs us that this gem is Manganaxinite with no significant Magnesioaxinite content.

Blue and Green Zoning in Manganaxinite, 2.16ct, Pakistan

SI 564, Drag

Manganaxinite gems with solid blue, solid green or solid orange body color were not found during the course of our study, but the existence of such gems is certainly possible.

Magnesioaxinite

The rarest species of gem Axinite is Magnesioaxinite - $Ca_2\mathbf{Mg}Al_2BSi_4O_{15}OH$. This is the only Axinite species that is allochromatic (colored only by impurities), and it was first identified in 1975 with the analysis of a pale blue gem from Tanzania (Jobbins, E. et al. 1975). Examples of Magnesioaxinite tend to be light in color, and all but two of the samples we tested fluoresce orange under longwave UV light. Magnesioaxinites that are near the pure endmember are weaky magnetic due to very low concentrations of iron and manganese, but examples with higher manganese content such as the pale-yellow gem below can show a strong magnetic response with floatation. The refractive index range (RI 1.656-1.678) of Magnesioaxinite is also lower than other Axinite species.

Yellow Magnesioaxinite, 0.81ct, Afghanistan
SI 267, Strong

Measured magnetic susceptibility values of Magnesioaxinite gems and crystals near the pure endmember are at the minimum measurable level at less than SI 20, indicating that a very small but detectable amount of manganese (> 0.13 wt% MnO) is present. No diamagnetic samples (SI < 0) were found. Our estimated magnetic susceptibility range for the Magnesioaxinite species is SI < 0 -275. Axinites with values higher than SI 275 would be primarily Manganaxinite in composition. Among samples in our study, we found little or no miscibility with Ferroaxinite within the Magnesioaxinite species, and no Magnesioaxinites with brown body color were found. Evidence of mixing between Magnesioaxinite and Ferroaxinite was found only within the Ferroaxinite species.

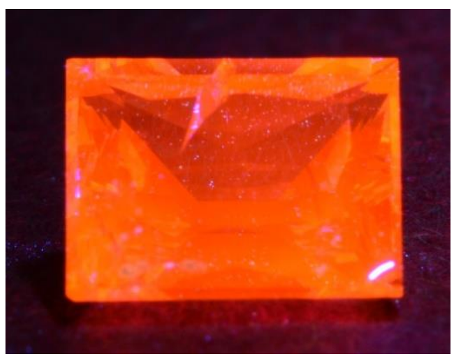
Since brown color from iron is mostly absent, other colors such as pink, lavender, blue, yellow, and orange become more apparent in Magnesioaxinite. These colors are due to small amounts of transition metal impurities such as vanadium and manganese (Mn^{2+} & Mn^{3+}). Magnesioaxinite can also be completely colorless.

The colorless Axinite gem shown below has the lowest measurable magnetic susceptibility (SI 17) of any Axinite in our study. A complete lack of color, in addition to low magnetic susceptibility and low refractive index (RI 1.656-1.665), are definitive indicators that this gem is Magnesioaxinite.

Colorless Magnesioaxinite. 0.7ct, Tanzania

SI 17, Weak

The absence of iron (Fe^{2+}), which inhibits fluorescence, permits Magnesioaxinite gems to fluoresce strongly under longwave UV light and weakly under shortwave UV light. As with Manganaxinite, the bright orange color of fluorescence is due to trace amounts of manganese (Mn^{2+}). The absence of a red color component in the fluorescence of this gem suggests chromium content is absent or too low to contribute red fluorescence.



Colorless Magnesioaxinte Fluoresces Strongly

Color zoning is evident in some Magnesioxinites such as the crystal shown below, which has pale pink body color and pale brownish orange color zoning. The pink color is produced by trivalent manganese (Mn^{3+}). This crystal is near the pure Magnesioaxinite endmember in composition and shows a very weak magnetic response when floated. It also shows strong orange fluorescence under longwave UV light.

Pink Magnesioaxinite, 6.3ct, Tanzania, 21 mm Tall

SI < 20, Weak

When sufficient blue color from vanadium is present, Magnesioaxinite can have pale blue or pale lilac (pinkish blue) color, as shown in the photo below (left). Lilac Magnesioaxinites with blue color can show distinct color change to pink in incandescent light, as pictured below (right). Unlike the pink crystal pictured above, the composition of the crystal below is somewhat removed from the pure Magnesioaxinite endmember. It is strongly magnetic (SI 139) due to greater mixing with Manganaxinite. The higher manganese content is unrelated to the blue color. This Magnesioaxinite crystal was incorrectly sold as Manganaxinite.

Lilac Magnesioaxinite, 5.6ct, 17 mm Tall, Tanzania

SI 139, Strong

The composition of another lilac Magnesioaxinite crystal shown below is even further from the pure endmember, with significantly greater Manganaxinite content. Higher magnetic susceptibility (SI 234) and a strong magnetic response when floated reveal that this Magnesioaxinite is approaching the composition boundary between Magnesioaxinite and Manganaxinite. Magnesioaxinites with pale lilac color can look similar to lavender Manganaxinites and can show similar orange fluorescence, but differences in magnetic susceptibility separate the two species.

Lilac Magnesioaxinite, 21.45ct, 22 mm Tall, Tanzania, Strong Orange Fluorescence

SI 234, Strong

Solid blue body color is very rare in Axinite, and we were unable to find any examples for this study. The crystal pictured below is a solid violet-blue Magnesioaxinite from Tanzania, as reported by a trusted source. Although we were unable to test this crystal and verify its identity, we include the photo here to show the potential range of body color found in Magnesioaxinite.

Blue Magnesioaxinite, 3.1ct, Tanzania

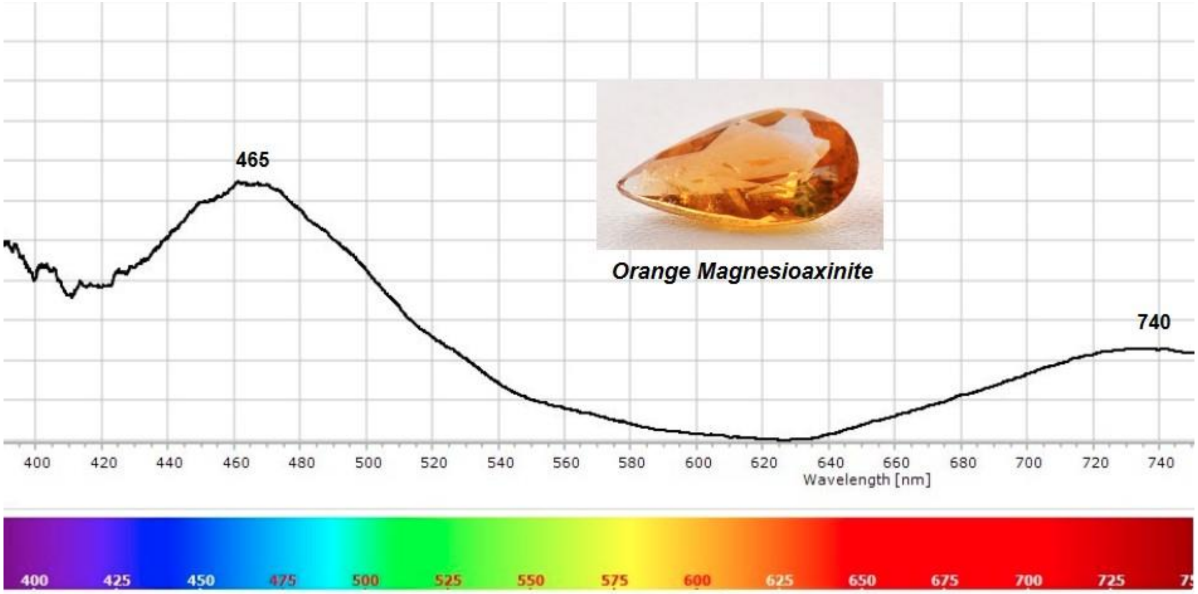
Photo Courtesy of Unlimite-Gems.com

Orange is another unusual color found in Magnesioaxinite. The pear-shaped gem pictured below has bright orange body color produced by a very small amount of manganese. We know the composition of this Magnesioaxinite gem is near the pure endmember because it is very weakly magnetic (SI < 20).

Orange Magnesioaxinite, 0.7ct, Tanzania

SI < 20, Weak

Magnesioaxinites with orange color have absorption spectra that are distinct from brown/yellow Axinites or lavender/pink Axinites. The absorption spectrum below shows broad peaks at 465nm and 740nm, which are almost certainly attributable to manganese (Mn2+). Transmission of light occurs primarily in the orange region of the visible spectrum near 620nm.



Absorption Spectrum for Orange Magnesioaxinite

The rough Magnesioaxinite crystal shown below has solid orange body color that is nearly identical to the gem above. But the chemical composition of the orange rough deviates significantly away from the pure endmember. This crystal has a measured magnetic susceptibility of SI 204 and shows strong magnetic attraction when floated. We can infer that the higher magnetic susceptibility is due to significantly higher manganese content from mixing with Manganaxinte. Mixing with Ferroaxinite is not indicated, as this crystal has no brown color and shows strong UV fluorescence.

Orange Magnesioaxinite, 2.25ct, Tanzania

SI 204, Strong

Another example of strongly magnetic Magnesioaxinite is shown below. This pale-yellow gem has high magnetic susceptibility (SI 272), and like the orange crystal above, its composition does not approach the pure Magnesioaxinite endmember. The predominant yellow color indicates manganese (Mn2+) from Manganaxinite. The measured magnetic susceptibility and lack of a Drag response verify the gem is primarily Magnesioaxinite in composition, but borders on Manganaxinite composition. Unlike all other Magnesioaxinites tested in our study, yellow Magnesioaxinites don't fluoresce, so we know that more than a trace amount of iron (Fe2+) from Ferroaxinite must also be present to inhibit fluorescence from manganese.

Pale Yellow Magnesioaxinite. 0.43ct, Pakistan

SI 272, Strong

Tinzenite

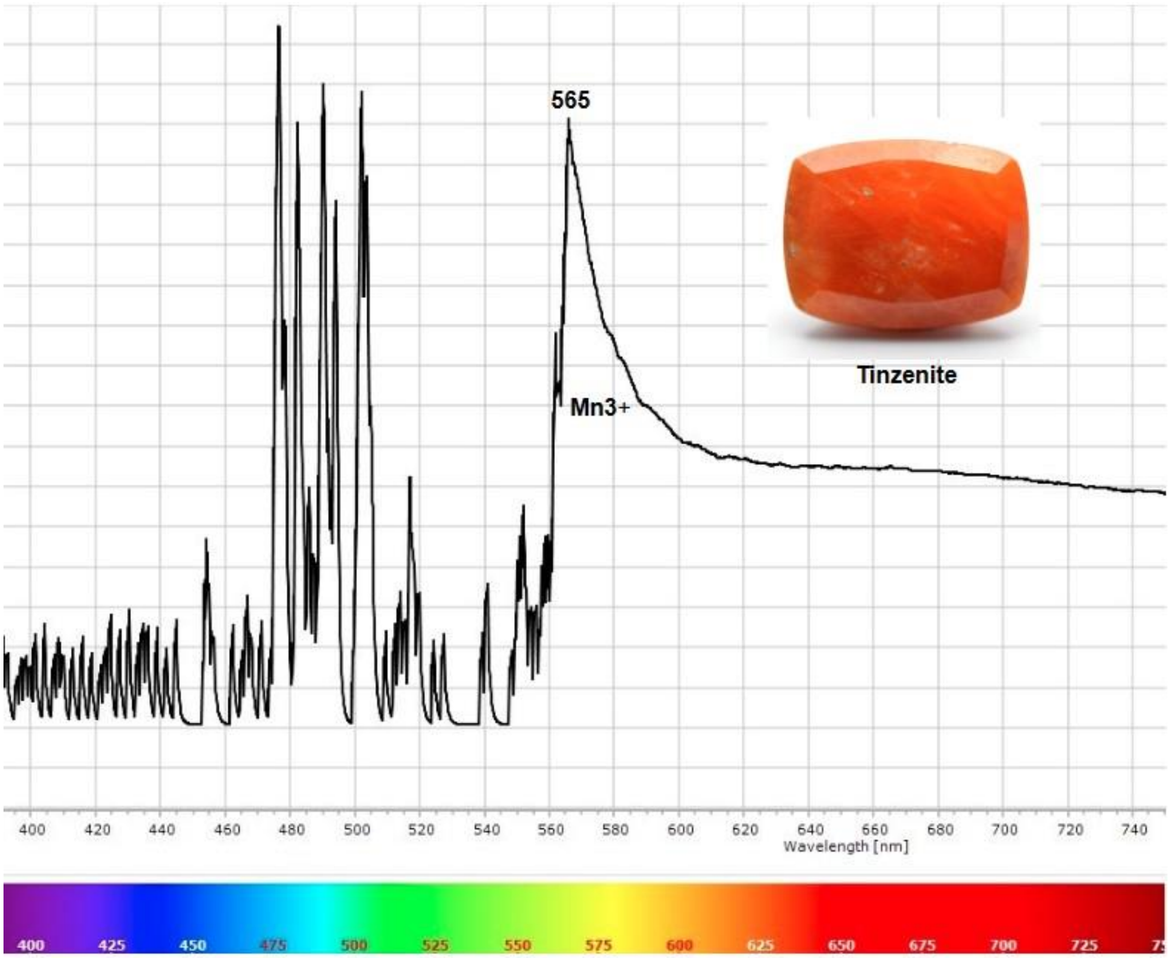
Tinzenite - Ca_2**Mn_4^{2+}** $Al_4[B_2Si_8O_{30}](OH)_2$ - is a yellow to orange idiochromatic species of Axinite that is found in only a few locations worldwide, and it is rarely faceted as a gemstone. When Tinzenite was first discovered in 1923, it was not recognized as an Axinite species at all and was assigned a different mineral name based on the location of its discovery near the town of Tinzen, Switzerland (Lumpkin & Ribbe, 1979).

Like Manganaxinite, manganese is the defining transition metal in Tinzenite. The difference is that Tinzenite has a much higher concentration of manganese than Manganaxinite, and as manganese replaces calcium, the proportion of calcium is lower than in Manganaxinite. We found that the unusually large translucent 10ct Tinzenite gem shown below is 3 ½ times more magnetic than most Manganaxinites due to the higher manganese content. The measured magnetic susceptibility (SI 1879) of this gem is equivalent to that of many Garnets.

The pure intense orange color suggests that this Tinzenite could be near the pure Tinzenite endmember in composition (> 20 wt% MnO), but we were unable to test other samples of Tinzenite for comparison. The absorption spectrum shown below suggests the color is largely influenced by trivalent manganese (Mn3+ peak at 565nm). Yellow color from bivalent manganese (Mn2+) plus red color from trivalent manganese (Mn3+) can produce orange color. Specimens of manganese-rich Tinzenite can be either yellow or orange (Milton, C. et al.,1953).

Translucent Tinzenite, 10.8ct, Val Graveglia, Italy

SI 1879, Drag



Tinzenite Absorption Spectrum Peaks at 562nm Indicating Mn3+

Due to large size and weight, the orange gem above shows only a Drag response, but Tinzenites with similar magnetic susceptibility can be expected to show a Pickup response when samples are under approximately 6ct. in weight. The high concentration of manganese (Mn2+) also raises the refractive index of Tinzenite to around RI 1.69-1.70, which is higher than the RI of other Axinite species. These identifying characteristics separate Tinzenite from other Axinites.

Tinzenite is in continuous solid solution with Manganaxinite, and many intermediate examples may exist (Grew, E., 2018), although such intermediates are rarely encountered as gemstones. The large orangey-brown gem below appears to be one such intermediate, and the absorption spectrum for this gem indicates manganese and iron content. The brown color component is likely due to a minor amount of iron (Fe2+), presumably from mixing with Ferroaxinite.

Manganaxinite-Tinzenite Intermediate, 9.2ct, Pakistan

SI 998, Drag

The gem above is over-dark and heavily included, yet transparent. It shows a Drag response and has a magnetic susceptibility of SI 998, which is less than our orange Tinzenite gem, but much higher than either Ferroaxinite or Manganaxinite. The abnormally high magnetic susceptibility informs us that this gem may be a Tinzenite-Manganaxinite intermediate, with a chemical composition that is a bit closer to Manganaxinite than to Tinzenite. The refractive index and specific gravity are slightly higher than what we have measured for Manganaxinite, but lower than for Tinzenite. Neither this intermediate gem nor the orange Tinzenite gem above fluoresce under UV light.

Questions of Color

Over the course of our study of magnetism and color in Axinite, we were puzzled by number of ambiguities about color in relation to manganese. Color theory is a complex field of physical chemistry, and information about causes of color within Axinite and many other gem minerals is incomplete. It is our hope that the answers to questions presented below will at some point be addressed by researchers who study gem color.

<u>Idiochromatic?</u>

Gemologists consider Manganaxinite to be an idiochromatic (self-colored) gem species, with bivalent manganese (Mn^{2+}) as the coloring agent inherent in its chemical formula. But as we have shown, bivalent manganese (Mn^{2+}) is a weak chromophore that can at times produce little or no color.

Two good examples are lavender Manganaxinites and pink Manganaxinites, in which Mn^{2+} fails to produce color even though it is present in high concentration. All visible color in lavender Manganaxinite appears to be the result of trace impurities of vanadium (blue color) plus tiny amounts of trivalent manganese (Mn^{3+}, pink color). In pink Manganaxintes that have no blue color component, trivalent manganese (Mn^{3+}) is the sole coloring agent. In the same way that Mn^{3+} generates pink color in Tourmaline, it is believed that Mn^{3+} in Axinite is converted from Mn^{2+} during crystal formation due to gamma radiation from radioactive decay.

Lavender Manganaxinite

Pink Manganaxinite

Neither vanadium (V^{3+}) nor trivalent manganese (Mn^{3+}) is represented in the chemical formula for Manganaxinite, and these coloring agents therefore act as impurities. In the absence of V^{3+} and Mn^{3+}, lavender and pink Manganaxinite would be colorless. By definition, allochromatic gems are colored entirely by impurities and colorless when pure. No completely colorless Manganaxinites have so far been reported, but we pose an interesting question: Are lavender and pink Manganaxinites allochromatic?

<u>Yellow Color</u>

A related question is: Is bivalent manganese (Mn^{2+}) responsible for all yellow color in gem Axinite, and if so, why is it inconsistent in creating yellow color? Mn^{2+} sometimes fails to create color even when in high concentration, yet at other times it is associated with yellow color. We did not find any yellow color in Manganaxinites that were near the pure endmember in composition, suggesting that yellow color could instead be linked to lower concentrations of manganese in gem Axinite, as we find in yellow-brown Axinites that contain a mixture of manganese and iron.

Or is it possible that an additional chromophore such as *intervalence charge transfer* is involved in inducing yellow color? We know that in yellow Tourmaline, *intervalence charge transfer* involving manganese and titanium (Mn^{2+}-Ti^{4+}) contributes to yellow color in addition to manganese (Mn^{2+}) (Rossman & Mattson, 1986). Does something similar occur in Axinite? Or could REE's (rare earth elements) that are present in Manganaxinite (Zagorsky, V. et al., 2016) act as sensitizers in concert with Mn^{2+} to trigger yellow color?

Yellow Manganaxinite

Or might trivalent iron (Fe^{3+}), or IVCT (*intervalence charge transfer*) involving trivalent iron (Fe^{3+}), be a source of yellow color in Axinites as it is in yellow Grossular and yellow Andradite (Topazolite) Garnets? Trivalent iron (Fe^{3+}) primarily occurs at octahedral sites in Axinite, as it does in yellow Grossulars and Andradites (Andreozzi, G. et al., 2004 & G. Sugitani, Y. et al., 1974). And the highest concentrations of Fe^{3+} in Axinite are to be found in yellow-brown Axinites that contain a mixture of Manganaxinite and Ferroaxinite.

We present these potential inducers of color only as theoretical scenarios to address the question of inconsistent yellow color in Axinite. To date, none of these color mechanisms have been proposed or documented to cause color in Axinite.

Orange Color

We can also ask: Why is manganese in Axinite sometimes associated with orange color rather than yellow color? Is orange color simply the result of yellow color from Mn^{2+} combining with pink or red color from Mn^{3+}? Yellow + pink or red = orange. And if so, does orange color appear in Axinite only when Mn^{3+} is present in sufficient concentration to add a pink/red color component? This appears to be the case with orange Tinzenite, where the optical absorption spectrum suggests that orange color is strongly influenced by Mn^{3+}. Is this also true for the Magnesioaxinite species, with orange color being triggered by available Mn^{3+}?

Orange Tinzenite Magnified

Or perhaps manganese isn't the only chromophore that produces orange color in Axinite? A possibility to consider is that *intervalence charge transfer* is involved. A recent study of orange Spessartine Garnet (Zhu, M. & Guo, Y., 2023) found that iron to iron (Fe2+-Fe3+) *charge transfer* contributes to orange color in conjunction with manganese (Mn2+). Could such a *charge transfer* process also occur in Axinite? Evidence of *intervalence charge transfer* is investigated primarily by optical and Xray absorption spectroscopy, and to date it has not been described or suggested as a cause of orange color in Axinite.

<u>Color Intensity</u>

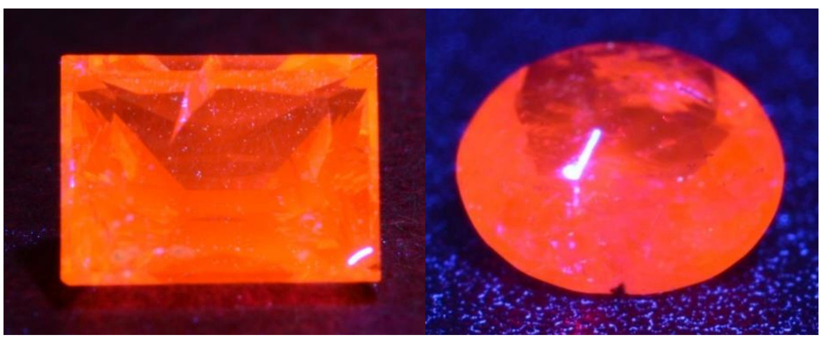
Yet another enigma of Axinite color is that the intensity of yellow and orange color associated with manganese (Mn2+) is not proportional to the concentration of manganese. How is it that the extremely low concentration of manganese oxide found in the orange Magnesioaxinite gem shown below (left), which likely approaches 0.13 wt% MnO, can create orange color that is equally as intense as orange color found in the Magnesioaxinite crystal shown below (right), which contains a much higher concentration of manganese oxide?

These Two Orange Magnesioaxinites with Similar Color Intensity

Have Markedly Different Concentrations of Mn2+

Likewise, strong orange color can occur in both Magnesioaxinite and Tinzenite, yet the concentration of Mn2+ in Tinzenite is vastly higher. This curious phenomenon is not unique to Axinite. We also see it in orange Hessonite Garnet and orange Spessartine Garnet, two species of Garnet that can have very similar orange body color from manganese even though the concentration of manganese is wildly different between the two species. Such examples suggest that *intervalence charge transfer* like that already noted for orange Spessartine might be involved, as IVCT requires only tiny amounts of transition metals to create intense color.

In a similar fashion, there is no direct relationship between the concentration of manganese (Mn2+) and the color intensity of orange longwave UV fluorescence activated by Mn2+. Only a few parts per million of Mn2+ are needed to activate visible orange fluorescence under longwave UV light (Haberman et al., 1997). We find that orange fluorescence in a completely colorless Magnesioaxinite appears just as strong as orange fluorescence in a lavender Manganaxinite that may contain as much as 100 times more manganese (Mn2+).



Colorless Magnesioaxinite (lft) Fluoresces Just as Strongly

as Lavender Manganaxinite (rt)

But when the concentration of Mn2+ reaches the much higher level found in our orange Tinzenite, it produces no UV fluorescence at all. Is the lack of orange fluorescence in Tinzenite due to concentration quenching by Mn2+? Again, we find a similar circumstance in Garnet. Moderate orange fluorescence from manganese (Mn2+) is seen in pale and colorless Grossular Garnets that may contain only trace amounts of manganese, but fluorescence is absent in orange Spessartine Garnet, where the concentration of manganese oxide (MnO) can reach as high as 41% (Deer, Howie & Zussman, 1962).

To our knowledge, none of our questions regarding gem color or gem fluorescence in Axinite have been specifically addressed or answered in published research. This concludes our report on Axinite. A list of references with links is presented below.

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