

MINERAL FLUORESCENCE AT BISBEE, ARIZONA



ARAGONITE, FLUORESCING A PALE BLUE, WITH A PARTIAL DOLOMITE COATING, FLUORESCING A NEAR-WHITE, ON MINOR, LIGHT GREEN FLUORESCING CALCITE UNDER SHORTWAVE-UV LIGHT, 7TH LEVEL SOUTHWEST MINE. SPECIMEN - 16 CM.

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Introduction:

Mineral fluorescence, that phenomenon whereby a mineral actually glows when exposed to ultraviolet light, is an important, but often overlooked aspect of the overall mineralogy of many mineral deposits. In some cases, a mineral continues to luminesce after the ultraviolet (UV) light has been removed, it is said to phosphoresce. Phosphorescent minerals are far less common than fluorescent minerals.

Fluorescence in minerals is caused in most cases by a wide range of usually invisible chemical elements or activators. These activators, either together or separate are usually present in small quantities. Fluorescence can be an important aid in mineral identification as well as be an indicator of the presence of otherwise non-apparent elements or telling an investigator more about the mineral and the deposit from which it came. Further, effects such as multiple hues or partial fluorescence can indicate unrecognized species or identify different phases of mineral deposition. These, and other aspects of fluorescence can reveal much that is not obvious without the use of ultraviolet light.

The intent of this discussion is not to be dissertation on mineral fluorescence, but rather an overview of mineral fluorescence at Bisbee, as recorded by the authors observations, experiences and our understanding of what we have seen. For more detailed information on fluorescence in general, the reader is referred to the voluminous on mineral fluorescence available through a number of well written sources. George Polman's fine web site gives a good list of such references it is at https://www.polmanminerals.com/html/recommended_reading.html However, some very basic information is provided here.

Historically, UV lamps for use with minerals were expensive (notably portable units), relatively delicate and not always easy to find. So much has changed of late and most of the earlier issues have been resolved. UV has always allowed a way to increase the information and enjoyment of studying minerals and now it is in general reach of any collector or scientist. We have long used UV in our study of Bisbee minerals and it has truly added new dimensions and vast information to investigative work.

There are commercially available four different UV wavelengths that are commonly used on fluorescent minerals. Shortwave (SW) (with a peak at 253.7 nm), Medium Wave (MW) (with a peak at about 312 nm), Long Wave 350 (LW350) (with a peak at about 352 nm) and Long Wave 370 (LW370) (with a peak at about 368 nm). The two LW wavelengths usually do not make that much difference in LW fluorescent minerals, so it can just say LW. However, some calcites and a few other minerals will fluoresce brighter under MW than under SW or LW (Don Newsome, personal communication, 2017). Of these, SW is the more commonly used, followed by LW, while the MW lights are largely restricted in use by the most dedicated fluorescent enthusiasts.

This is an evolving science as lights with more wavelengths are becoming reasonably available and affordable. Thus, it should be expected that, with time, more information regarding the fluorescence of Bisbee minerals will come.

For this study, SW was principally used because of the then ready availability of very powerful units for field work and high-quality smaller units for laboratory application. LW was restricted to laboratory study, inasmuch as access to some of the underground areas studied in the past was no longer possible 20 + years later when LW lights became more available. As will be noted, surprisingly few of the $\pm 7,000$ Bisbee specimens studied responded to LW light.

Photography of specimens and areas underground with UV light is not a simple venture. A bit on the techniques used, both in the laboratory and underground to better understand the illustrations herein. Capturing true color and intensity while providing visual information on the whole specimen under all spectrums is challenging, but absolutely vital. The use of photo enhancing software is generally not acceptable. That being said, we have merged photos, as will be noted with each photo so treated and, on occasion, used a sharpening tool to better define detail, particularly edges as the glow of fluorescence makes crystal edges decidedly less distinct. All applications require carefully monitoring for any color shift.

Underground photography required very long exposures, often several minutes or more, in spite of the use of a powerful light. In all cases, the walls, floor, ceiling were “painted” with the UV light, by moving the light around; painting all areas with the light, exercising care to allow equal time of illumination, as well as assuring the distance from the light to wall, floor and ceiling is the same to have equal exposure. When a person is in the photo, only white light is used for illumination of the person and the area immediately adjacent and illuminated last.

As the mine areas were wider and or taller than a 50 mm lens can accommodate, a photo merge tool was used in Photoshop CS6 to create a panorama. **No** other photo editing applications were used in these photos. This is a technique we have long used, with great success, in underground photography.

In the laboratory, a similar approach was used, whereby the specimens were illuminated by moving the UV light around the specimen. Another difference from other photographers, was taking the photographs in low light, not total darkness, so that the whole of the outline of the specimen can be seen. This also allows for the nonfluorescent minerals on the specimen to be seen, albeit less than fully.

It is our considered opinion that this somewhat different approach to photography, both in the field and the lab, is a much better way to provide more accurate images and, thus important information.

Mineralization:

Fluorescence is all about the chemistry of the minerals. Some minerals are naturally fluorescent due to the primary constituents, while the inclusion of other elements (activators), often more than one, within the mineral may combine to cause the response. In many instances the amount of other included elements to render the fluorescence is meniscal; a parts per billion level can be sufficient in some cases. Conversely, too much of an element may well quench any fluorescent response, as will even minor amounts of other, usually metallic elements. Thus, a brief review of the complex mineralization at Bisbee may be helpful.

To fully characterize the nature of Bisbee's fluorescent minerals, it is essential to briefly touch on the mineralization of the deposits in a most general manner. Bisbee, or the Warren Mining District, is an intensely mineralized area, which underwent at least four pulses of hypogene (primary) mineralization and several, widely separated periods of supergene oxidation activity (secondary).

The minerals were originally deposited 200.0 ± 0.8 Ma, more or less contemporaneously with the emplacement of the various intrusive units, which make up the Sacramento Stock Complex (Lang et al., 2001). They were emplaced as numerous modest sized to very large sulfide, carbonate replacement deposits scattered throughout the Paleozoic limestones (Bryant & Metz, 1966, Graeme, 1981).

Multiple mineralizing episodes ensued, first deposited were huge amounts – hundreds of millions of tons - of iron/sulfur/silica then large amounts iron/copper/lead/zinc/sulfur, followed by iron/lead/zinc/sulfur and finally by an overprinting of very modest amounts of gold, silver, tellurium, bismuth, tin, tungsten, vanadium, arsenic and antimony. The result of the presence of these many elements was a very broad suit of hypogene minerals, with most occurring as minor to rare accessory minerals associated with the massive pyrite/silica deposits as well as the copper, lead or zinc sulfide ores (Graeme, 1993). These sulfide deposits were quite compact; faithful to the replaced limestone with very few voids present.

In addition, the hosting limestones as well as the several intrusive units were altered to varying degrees by the presence and passage of the hot mineralizing fluids. A number of different minerals were formed by these hydrothermal fluids as they made their way through the rocks. Often, very minor amounts of elements were hydrothermally deposited in the older, pre-existing rocks.

As erosion removed the overlying rocks in pre-Cretaceous times, oxidation of some of the sulfide orebodies took place, but was stopped by burial with more than 1,500 meters of Cretaceous sediments. With Pliocene times came the region-wide normal faulting of the basin and range type, which formed the major topographic features so evident today. During the development of the basin-and-range features, the entire Mule Mountains were tilted to the northeast some 30° followed by uplift. Uninterrupted erosion since that event has stripped the Cretaceous sediments from the western portion of the mineral deposits and allowed supergene alteration to resume in this area. It was largely during this last, prolonged period of supergene activity that most of the minerals for which Bisbee is so famous were formed. There, are several areas where the pre-Cretaceous supergene activity formed superb mineral specimens with little to no influence from later such events.

One of the more common supergene mineral environments of note were the abundant oxidation caves, which formed as the ores shrank during oxidation due to the removal of the contained sulfur and much of the iron (Graeme, et al., 2016a). Copper was deposited both in the caves and below as rich carbonate orebodies, with abundant cuprite and elemental copper in the clays. Both aragonite and calcite were common in these caves, some of which was fluorescent. As supergene activity occurred over an extended period with changes in the solution chemistry in some cases, it was not uncommon to find specimens in these caves with partial fluorescence reflecting changes in solution chemistry.

In and surrounding the oxidized orebodies, numerous voids formed. Many, if not most of these were soon lined or filled with oxide zone minerals, of which calcite was the most common. Oddly, little, very little of this supergene calcite is fluorescent. The solutions which transported the varied elements and deposited the supergene minerals in these voids during oxidation was undoubtedly a multi-element soup, which often varied over time, as manifested by the different species present and their paragenetic relationship.

All of these factors resulted in more than 330 distinct mineral species have been confirmed from here making Bisbee one of the most mineralogically diverse localities in the world. Of these many species, only 15 are recognized as fluorescent.

Bisbee, the collecting culture:

The apparent paucity of fluorescent minerals may be, at least in part, due to a lack of interest. It would seem that almost no one at Bisbee collected fluorescent minerals. In our combined 60+ years of collecting Bisbee, we have only met two Bisbee collectors that actively acquired fluorescent minerals for his/her personal collection and then only as a minor subset of their main collection. While a few fluorescent minerals were also collected by several miners in 1947-48, this was to sell to mineral dealers who continually passed through this small town in their search for sales stock (Melvin Elkins, personal communication, 2016).

At first glance, this seems strange, given the strong propensity of the locals to collect minerals. The reasons lay in the strikingly beautiful copper carbonates and copper oxide zone minerals available for most of Bisbee's 95 years of mineral specimen production. These were what the local collectors wanted, cherished and saved.

Indeed, few places in the world can lay claim to a culture more dedicated to collecting of the local minerals such as Bisbee. During the first half of the 20th century, in a town of 10,000+ souls, there were easily 500 – 600 collectors of varying degrees of sophistication, enthusiasm and quality of specimens within the collection. Collections of extraordinary quality were to be found on display in banks, bars, barbershops and gas stations. Wherever the miners did their business, there were collections of Bisbee's mineral classics to attract clientele, but more often than not, the business owners were avid collectors in their own right. Of course, mineral collections were to be found in many resident's homes and not just miner's homes, some of which were extraordinary.

However fluorescent minerals were never a part of public collections nor, as noted, of the vast majority of private collections. This near total exclusion was a factor of several very obvious reasons. First, how can rocks that glow under expensive UV lights compete with the stunning natural beauty of the copper carbonates? As the early UV lights were relatively expensive, and the portable units even more so and often bulky, why invest in something that would add little to one's collection, so few did. A lack of interest in fluorescent minerals resulted in few specimens saved.

And too, the mineral species at Bisbee which tend to fluoresce – calcite, aragonite, sphalerite, etc. were either so common, if not ugly, who wanted them? Calcite, unless colorful, was largely ignored by the miners and local collectors for most of its history, as it was incredibly abundant at

Bisbee. Therefore, it was vastly underappreciated, such that when and if collected, specimens were generally mistreated and damaged. Most calcite specimens were sent to the garden as decorations, though a few, did find refuge in the collections of a few, more discerning collectors.

Bisbee's fluorescent minerals:

As noted above, this paper is intended to be just an overview of those fluorescent minerals encountered during the 60+ years of studying Bisbee's minerals by the authors, in both the field and lab. It must be stated at the outset that all of the species recognized as fluorescent and the variations of fluorescence within the species, as reported herein, is based on our extensive field work and specimens from our personal collection of 7,000+ Bisbee mineral specimens.

The abundant literature on Bisbee or on fluorescence referencing Bisbee has been reviewed with the few species note as being present at Bisbee being confirmed. Also, no additional species have been seen in the hundreds of collections studied worldwide. Please note that little effort was made to check for fluorescence in other collections viewed, as it is not a simple matter to do so.

We recognize that this restriction is a clear weakness in our work. Thus, there can be little doubt that other fluorescent species and/or variations in color response of recognized fluorescent species are to be found in other repositories. We encourage the owners of Bisbee specimens to explore their own specimens and expand upon this little-known aspect of what is surely America's greatest mineral locality.

The fluorescent minerals of Bisbee, an overview:

The often-spectacular fluorescence and the wide distribution of fluorescent minerals in the mines at Bisbee is not well known. Locally, small areas have produced material that is as vivid in fluorescence as that from most any other locality.

At Bisbee, this is particularly true in hypogene calcite, where the presence of divalent manganese is only evident by the vivid fluorescence, yet it is abundant and widely distributed. Manganese was added in varying amounts to much of the hydrothermal calcite during mineralization, which occurred during hydrothermal alteration. Such calcite was literally everywhere and is the source of fluorescence in the calcite cementing a limestone breccia, as shown in Figure 1.



Figure 1: Hydrothermal calcite cementing a limestone breccia, 3rd level, Southwest Mine, specimen - 13 cm.

The hosting limestones were also locally manganese enriched during hydrothermal alteration, resulting in whole or part beds fluorescing (Figure 2), depending on the amount of manganese emplaced, as too much will quench fluorescence as will the presence of other metals; notably iron and copper. Hewett and Rove (1930) found instances where the limestone contained up to 16% manganese. The degree to which this manganese enrichment developed fluorescent materials cannot be determined, but is sure to be significant.



Figure 2: Hydrothermally altered Martin limestone and hydrothermal calcite, both fluorescing red, with minor surficial supergene calcite, fluorescing green, under SW light, 3rd level, Southwest Mine. The view is looking down the main Queen Tunnel. The distant green light is for rail traffic control. Vertical view 2.8 meters This photo is a merged panorama, with no other Photoshop applications used.

As previously noted, only 15 of the 330 + species known from Bisbee exhibit fluorescence, yet the color range and intensity are often remarkable. The species from the district that are known to exhibit fluorescence are listed below:

<i>aragonite</i>	gypsum	quartz
<i>calcite</i>	hemimorphite	scheelite
<i>cerussite</i>	hydrozincite	<i>sphalerite</i>
dolomite	opal	uranopilite
fluorite	powellite	willemite

Table 1: Fluorescent minerals recognized at Bisbee, those in italics respond under both SW and LW light, while the plain text reflects SW fluorescence only.

While a wide variety of colors has been noted among the fluorescent minerals at Bisbee, red, red-orange and green are decidedly the more common. Calcite of hydrothermal origin typically responds with some hue of red to red/orange, though not exclusively. Several of the supergene

species, such as calcite and some gypsum usually respond with a yellow/green in fluorescence, suggesting that it is highly probable that uranium is the activator for this color, given its abundance.

Uranium-bearing species have long been recognized from the district (Bain, 1952; Hutton, 1957). Underground radiation measurements made by the authors revealed some areas where radioactivity levels were in the hundreds of counts per minute. At one time, the owners of the mines unsuccessfully sought a permit to recover uranium from water already being pumped from the mines for copper recovery.

Certain, mineralized areas in the mines at Bisbee exhibit broad zones of fluorescence due to a local abundance of intermixed, fluorescent species. One such place is above the “B” level of the Copper Queen Mine in a zone of hydrothermally altered limestone with abundant hydrothermal calcite, highly fluorescent sphalerite and spotty supergene hydrozincite on some of the oxidized surfaces. While somewhat limited in size, it is striking in appearance as can be seen in Figure 3 at the right.

To be sure, the distribution of fluorescent minerals in the district, as noted herein, is limited by the access to only a small fraction of the areas mined. Thus, this review cannot be considered as comprehensive. A brief discussion of the fluorescence of those species that are the most significant is offered below.

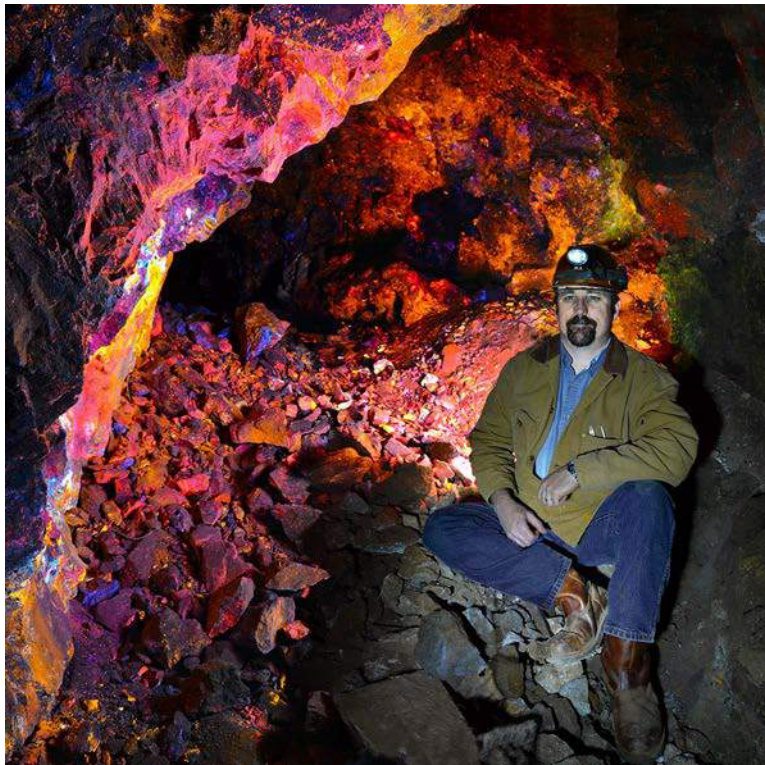


Figure 3: A highly fluorescent area on the “B” level, Copper Queen Mine with sphalerite and hypogene calcite responding to shortwave ultraviolet light. The area to the right is fluorescent as well, but illuminated by white light only. This photo is a merged photo of two to include the left side, with the person in the same place, in both. No other photo editing applications used.

THE FLUORESCENT MINERALS:

Aragonite: Aragonite was an abundant, widely distributed mineral throughout the district, with its most common occurrence in the many caves as speleothems. While abundant, relatively little fluoresces.

The most impressive material is from a small oxidation cave on the 6th level of the Southwest Mine, which fluoresces a bright, almost emerald green. The material occurs as either botryoidal masses (Figure 4) or intergrowths of acicular crystals to 5 cm. on botryoidal calcite (Figure 5). This material was locally abundant, but decidedly unattractive as a mineral specimen so very little

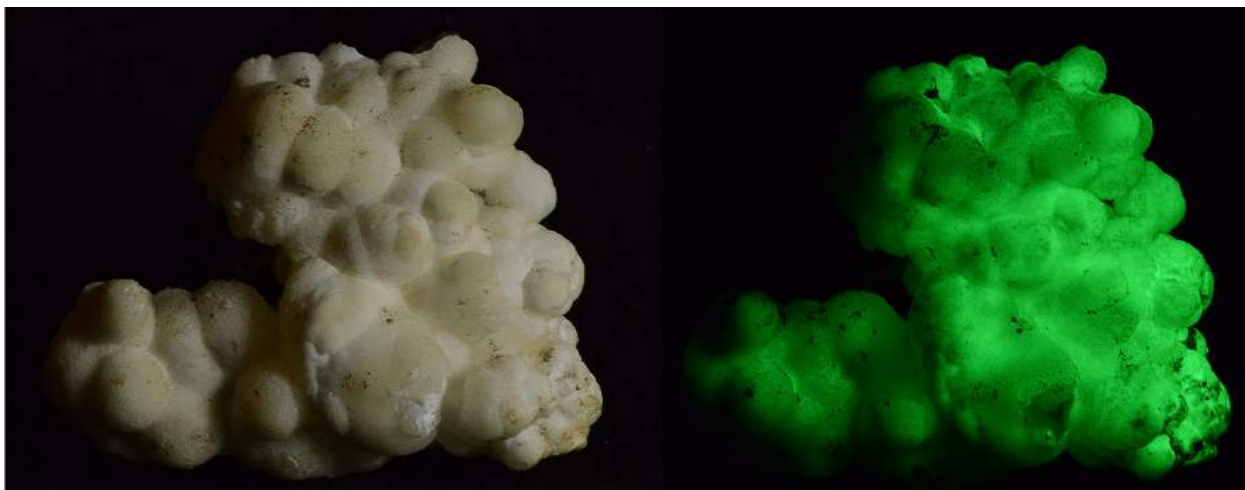


Figure 4: Botryoidal aragonite, right under SW light, 6th level, Southwest Mine, specimen - 7 cm.

was collected. Aragonite from several other localities will fluoresce a light yellow green or light blue.

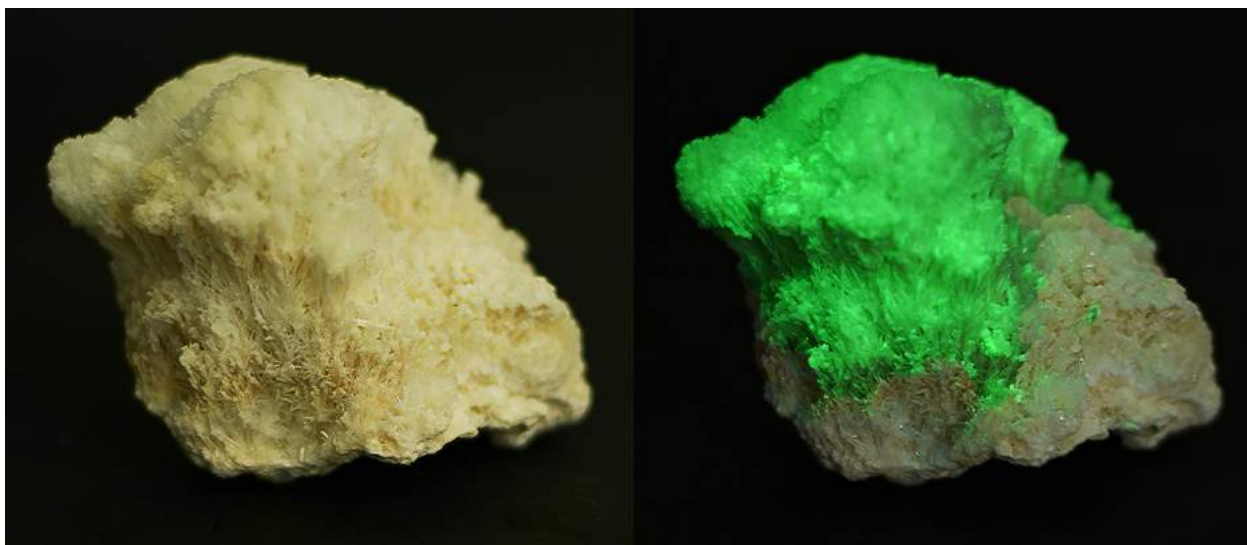


Figure 5: Aragonite on botryoidal calcite, from a small oxidation cave on the 6th level of the Southwest Mine, specimen - 6.5 cm. right - under SW light.

A much larger oxidation cave on the 7th level of this same large mine yielded a number of exceptionally fine aragonite specimens of chisel-like crystals to 5 cm, with minor dolomite, which fluoresces a lovely light blue (see the cover and Figures 6 and 7) and a red/light-purple under LW as shown in Figures 8 and 10. A similar light blue response to SW UV light was seen in otherwise rather unattractive specimens of botryoidal aragonite from yet another oxidation cave in this most prolific mine (Figure 7).



Figure 6: White to colorless, aragonite crystals with minor tan dolomite, on non-fluorescent botryoidal calcite, left under white light and right - under SW light, 7th level, Southwest Mine, specimen - 20 cm.



Figure 7: Botryoidal aragonite with very minor calcite, left under white light and right - under SW light. The calcite fluoresces green, the aragonite light blue, 6th level, Southwest Mine, specimen - 17 cm.



Figure 8: White to colorless, aragonite crystals with minor tan dolomite, left - under white light, center - under SW light, right – under LW light, 7th level, Southwest Mine, specimen - 3 cm tall.

Calcite: Calcite is one of the most abundant minerals at Bisbee, in both supergene and hypogene environments, which will be discussed separately. In supergene settings, it was most common as the often-magnificent speleothems, often copper-tinted, in the many, many oxidation caves and as pockets of well-formed crystals in and adjacent to the oxide ores. In the ores, calcite was often associated with copper minerals such as malachite, and cuprite, yielding spectacular, classic mineral specimens, most of which are not fluorescent. The presence of native copper is different, however, as will be discussed later.

Supergene calcite is pervasive in the oxidized zones, which may compose nearly half of the mineralized area mined underground. Several depositional environments for supergene calcite are common, with each variation presenting generally differing fluorescence. Multiple depositional periods are typical of most calcites from the supergene environments, as it was a continuing process over time, often extended periods and under subareal and sub-aqueous situations. Though abundant and pervasive, only limited amounts of supergene calcite fluoresce under SW light and even less under LW light, something which surprised the authors.

Cave speleothems were everywhere – literally everywhere in the totally oxidized zones (Graeme, et al., 2016) and are largely subaerial in deposition. When fluorescent and under SW these speleothems usually responds with varying tones of yellow-green, however other responses have been observed on rare occasion. LW light rarely elicits any response. A layered mix of non-fluorescent calcite with fluorescent calcite is relatively common, with SW light, as is partial fluorescence, undoubtedly reflecting differing solution chemistry and/or several periods of deposition.

Speleothem growth in most of the many hundreds of isolated oxidation caves was generally an ongoing, varying process over extended periods of time. Changes in the solution chemistry forming the speleothems is obvious from the variable copper/iron tinting so common in the abundant speleothems in the oxidation caves. Also, fluctuating solution levels, over time, were evident in many of these caves and cavelike openings with crystalline calcite levels serving as

markers for historic solution levels. Speleothem coloring and a wide range of supergene minerals in the caves reflect that varied solution chemistry entering these openings was often noted.

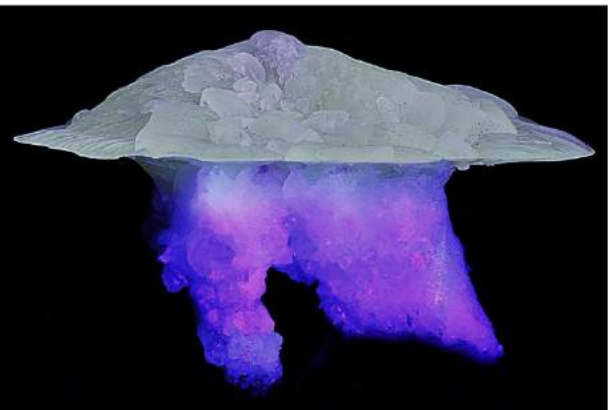


Figure 9: Botryoidal calcite from an oxidation cave, 6th level, Southwest Mine, specimen - 8.7 cm.



Figure 10: White and tan calcite/aragonite reflecting a solution line resulting from the partial flooding of the void by solution with different chemistry, as manifested by the varying response to UV light.

Top left – under white light. Lower left under SW light. Lower right under LW light. Specimen 8.7 cm tall, 7th level, Southwest Mine.



Supergene calcite from the oxidation caves, which formed under subaqueous conditions responds differently, when fluorescent. The flooding of these openings over geologic time, left crystals at and below the solution level, developing a horizontal line of crystals at the solution level. Often, several relic solution lines were present, reflection either more than one flooding event or fluctuating levels of a single event over time.

Generally, the subaqueous calcite from caves responds blue-white under SW light and yellowish to a curious greenish/yellow to blue/white/pink hue under LW light.



Figure 11: White to near-colorless calcite from an oxidation cave, reflecting a flooding event and the subaqueous deposition of crystalline calcite. Left – white light, center - SW light, right – LW light. Specimen 9.5 cm, 7th level, Southwest Mine.



Figure 12: Calcite deposited by flooding of a small oxidation cave. It grew in a sub solution environment on the cave walls.

Left, – white light, lower left - SW light, lower right – LW light. Specimen 10.2 cm, 7th level, Southwest Mine.



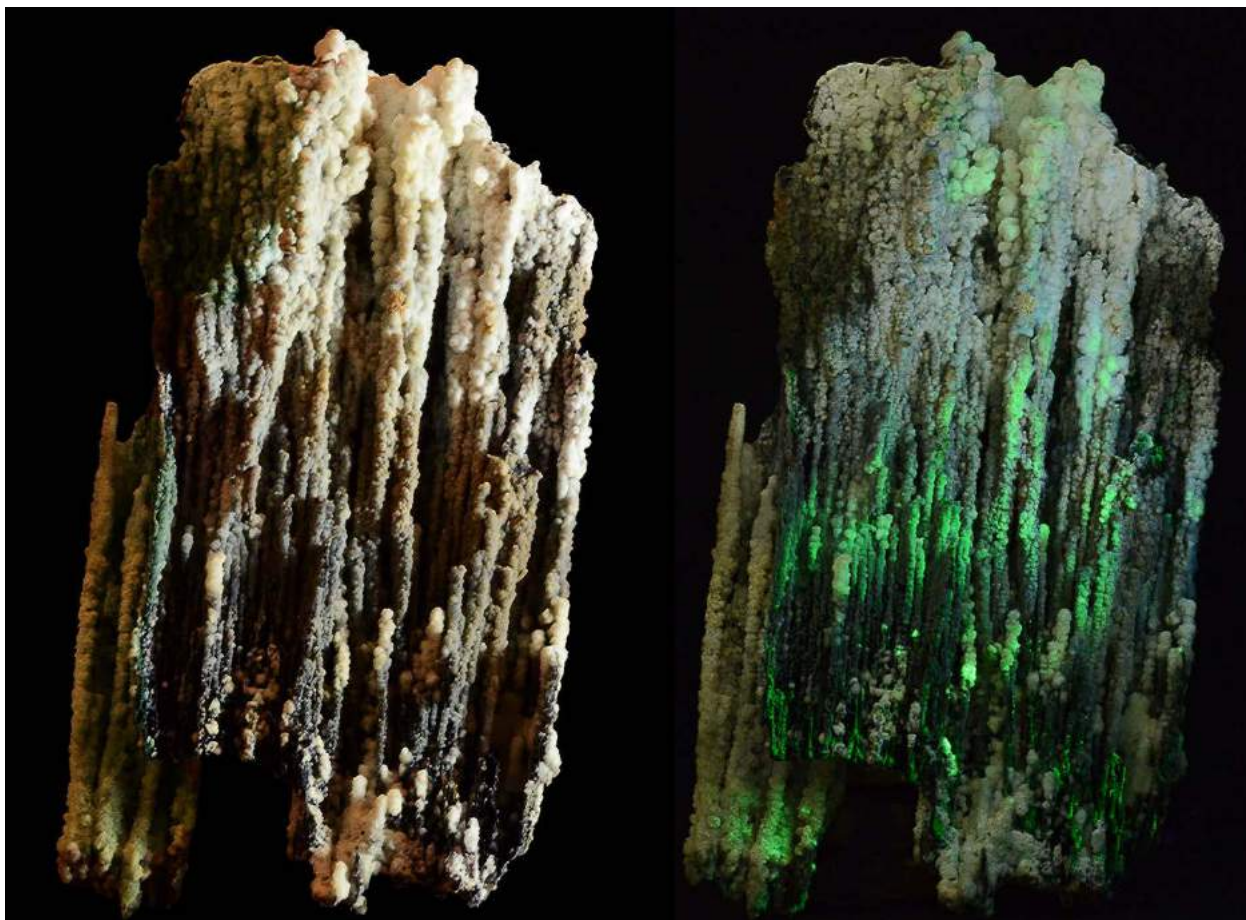


Figure 13: Botryoidal calcite with partial fluoresce, coating stalactitic goethite, 6th level, Southwest Mine; left - under white light, right - under SW light, specimen - 17.3 cm high. It is highly probable that the fluorescent material reflects a late-stage depositional episode, which chemically varied from the earlier event. Without the aid of fluorescence, this significant paragenetic feature would not have been discernable.

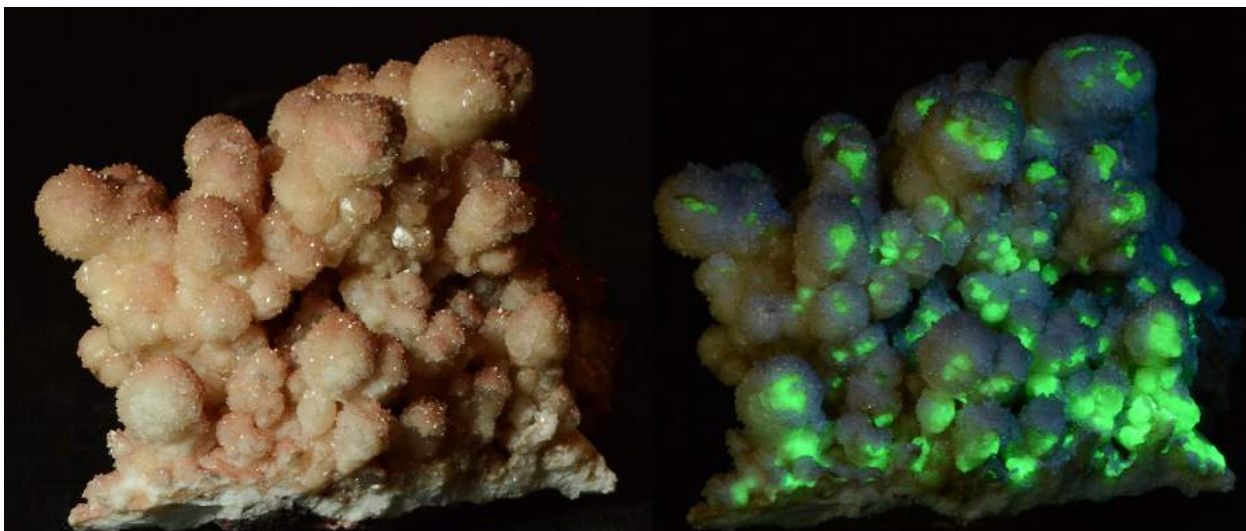


Figure 14: Fluorescent, botryoidal calcite of subaerial deposition environment, largely coated by a non-fluorescent layer of late-stage, crystalline, subaqueous calcite, deposited, when the small cave was flooded by CaCO_3 rich solutions. From the 6th level, Southwest Mine, specimen - 8.7 cm.

Voids with supergene calcite in and adjacent to the many oxide orebodies were everywhere. These openings were frequently calcite lined and many of Bisbee's astonishing calcite classics with malachite and cuprite were found in these environments. For the most part however, the calcite found in these vugs was not anything significant in the least. This study has shown that very little supergene calcite associated with the oxide ores is fluorescent. An example of a reasonably typical oxide ore mass with colorless to white calcite with malachite lining voids in goethite and hematite is shown in Figure 15 below.



Figure 15: Calcite with malachite lining voids in oxide ore. View – 3 .5 meters. 5th level of the Southwest Mine.

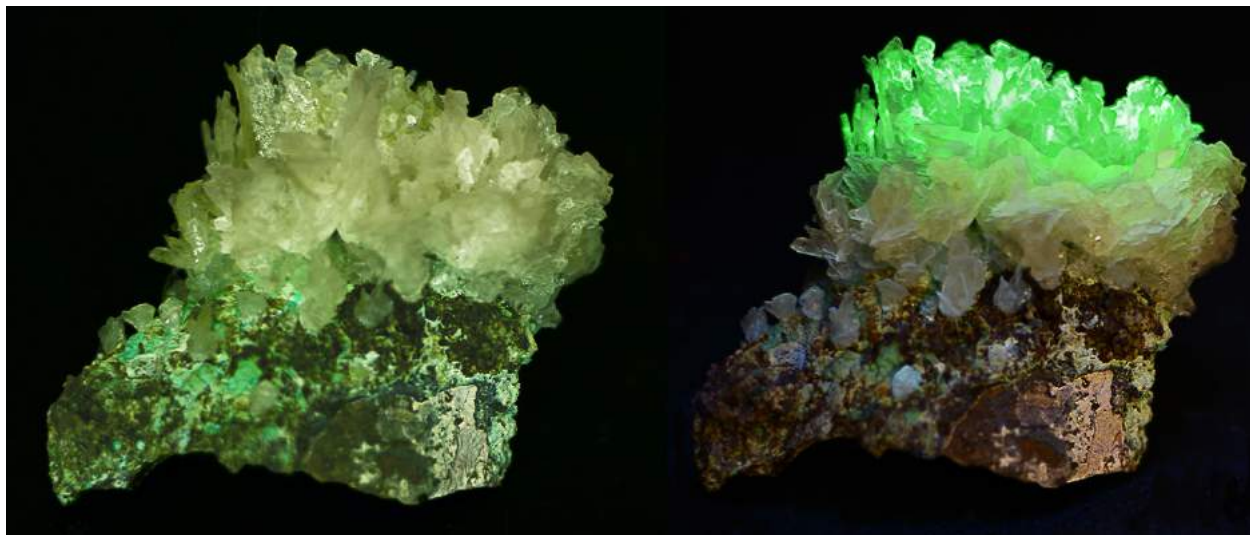


Figure 16: Calcite with aurichalcite on limestone, with only the top part of calcite fluorescing on the right - under SW light. The lower, non-fluorescent calcite is of a slightly different morphology, strongly suggesting perhaps a different depositional period and/or environment, as does the variable fluorescence. Further, the lower and earlier calcite is tinted ever so slightly green by contained copper, which may have quenched the fluorescence. Specimen - 11 cm. From a limestone collapse breccia on the 5th level of the Southwest Mine, which is shown in figure 17, below.

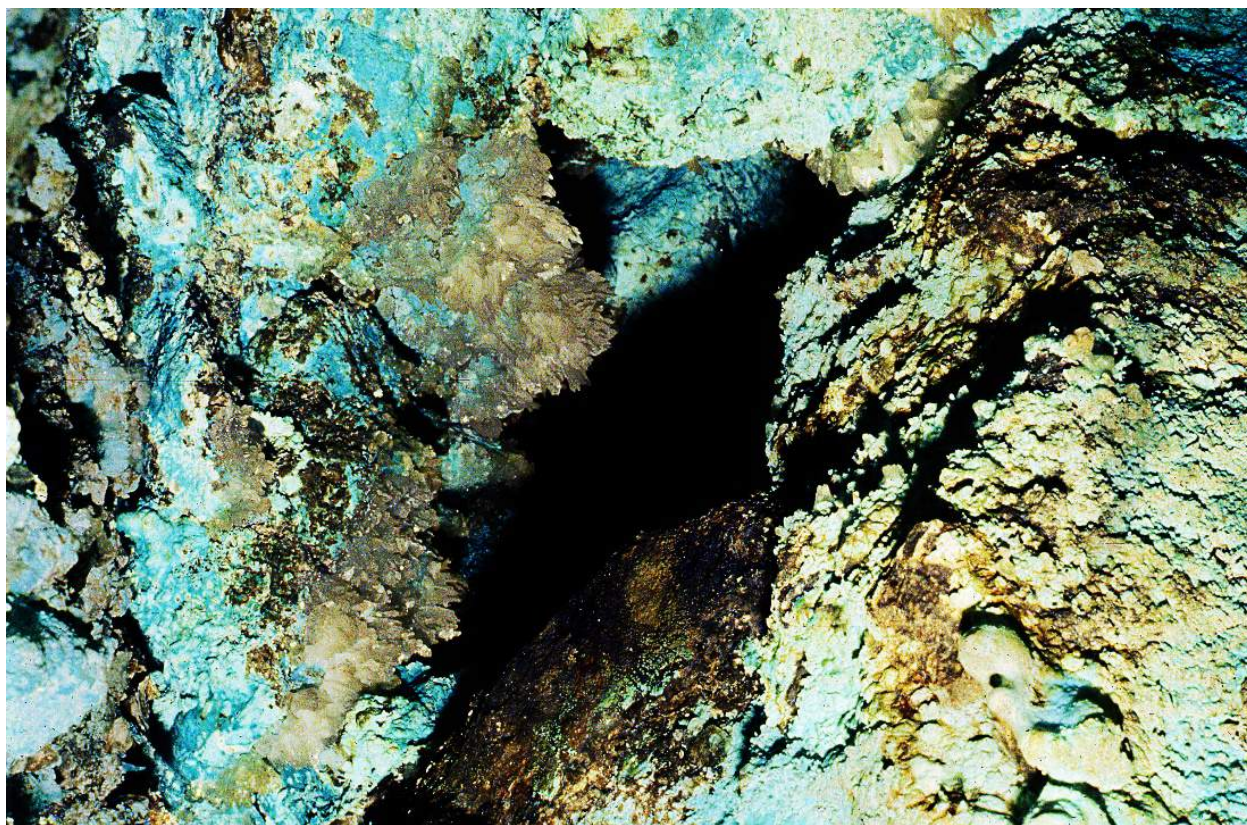


Figure 17: Dust-covered calcite with aurichalcite in a limestone collapse breccia that was the source of the specimen shown in Figure 16. View 80 cm, 5th level of the Southwest Mine.

A very modest amount of supergene calcite, which will respond with an orange hue or a near-white color under SW, has been found associated with some of the oxidized copper orebodies (Figure 18).



Figure 18: Calcite with malachite on goethite with only the early calcite fluorescing orange (right) under SW light, B level, Copper Queen Mine, specimen - 6 cm. Here too, excessive present copper may well have quenched the fluorescence

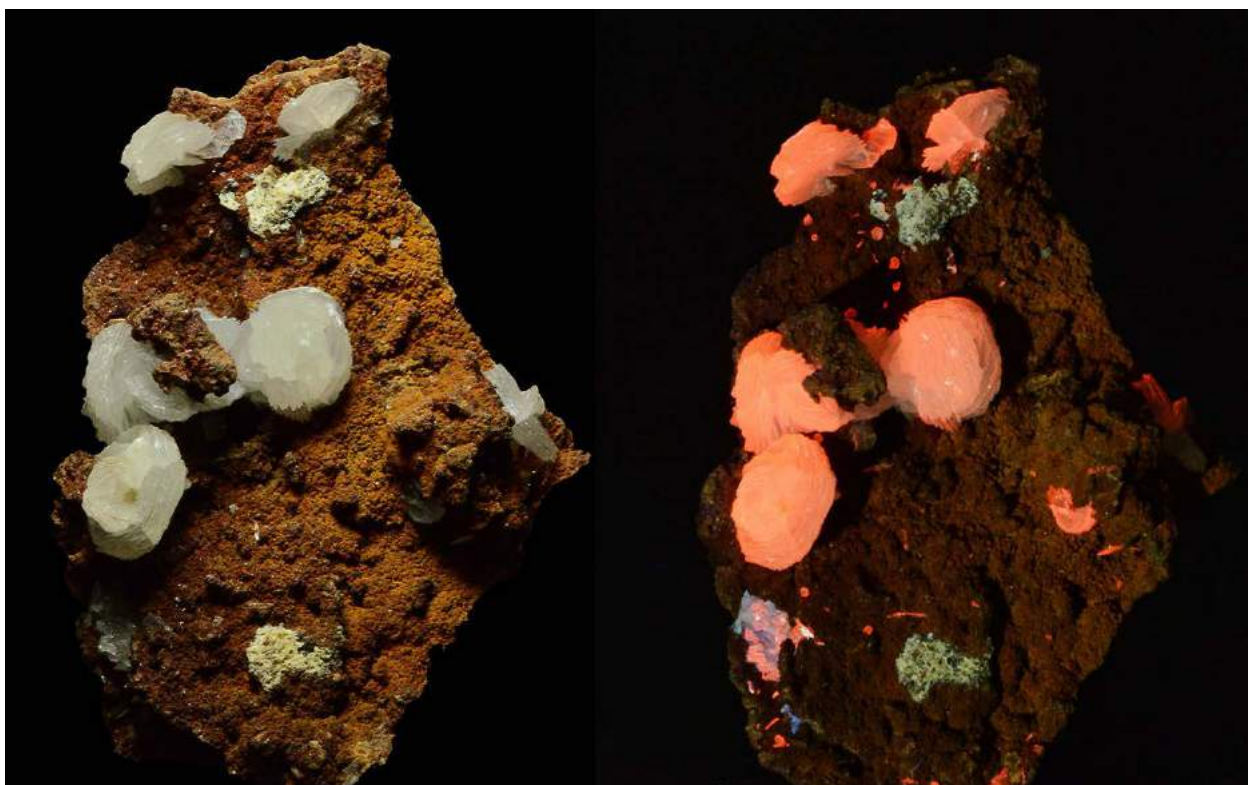


Figure 19: Subaqueous deposited, supergene calcite on goethite with the crystalline material fluorescing red/orange, while other splotches of probably subaerial calcite, seemingly later, fluoresce a dull gray/green under SW light (right), Cole Mine, specimen - 7 cm.

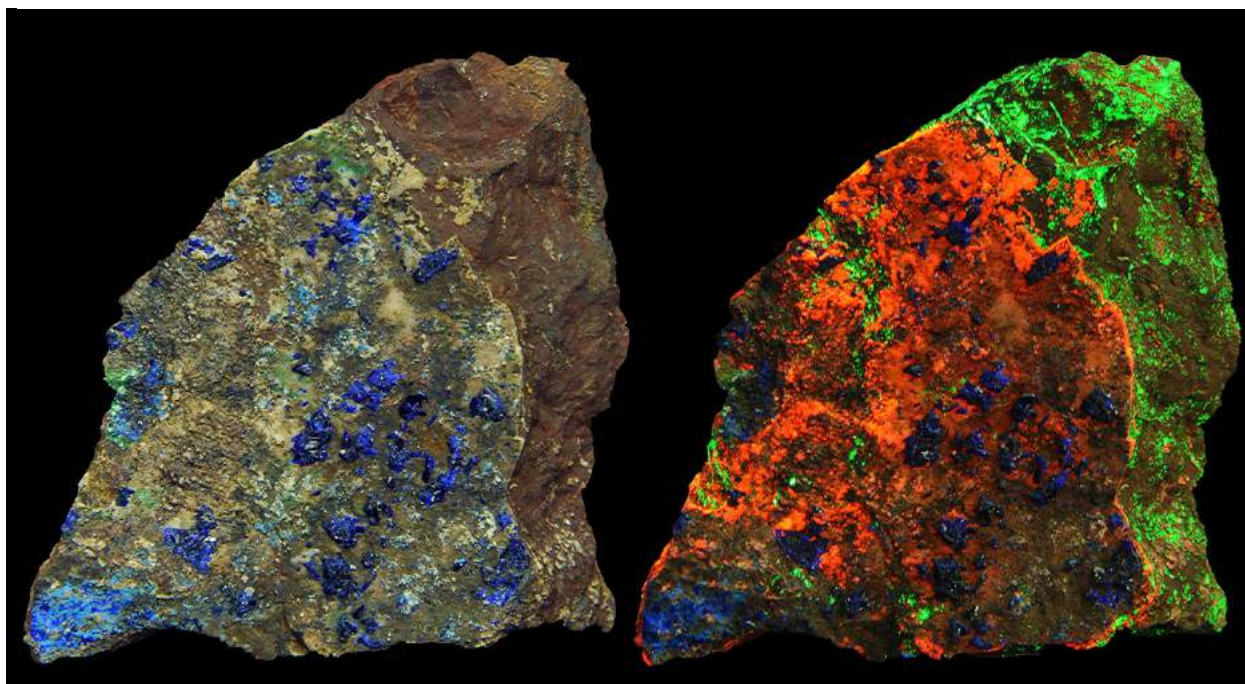


Figure 20: Supergene calcite fluorescing red/orange with nonfluorescent azurite on a mixture of willemite (strong green) and nonfluorescent, unidentified manganese oxides under SW light (right), substantial native copper was associated with the rich ores in this stope, which may account for the red response which is invariably seen with Bisbee copper/calcite specimens. Cuprite stope, Tunnel level, Higgins Mine, specimen – 6.5 cm.

As noted above, surprising little supergene calcite associated with the oxide ores fluoresces. There is one remarkable exception and that is the consistent, strong red-red/orange response of calcite associated with native copper, something clearly supergene in origin. The several dozen specimens of calcite in our collection associated with copper; **all** fluoresce a remarkable bright red/orange to red under SW. This is not true for LW light however. Typically, the copper was paragenetically earlier, occasionally with some of the copper included in calcite which was often bright and unoxidized. Any copper which was not protected by inclusion within calcite invariably had the typical patina from oxidation.

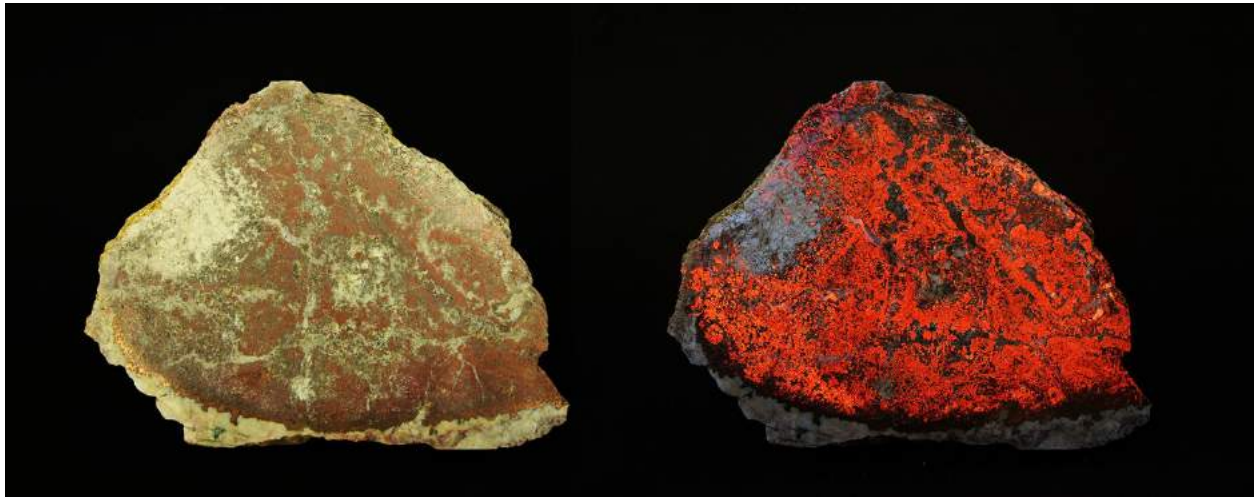


Figure 21: A polished slab of supergene calcite completely encasing spongy copper with quartz under SW light (right), 1900 level, Campbell Mine, specimen - 17 cm. Locally, this material is often called “campbellite,” particularly when more cuprite and/or malachite is present. However, the presence of cuprite and/or malachite does not appear to dampen or affect the fluoresces of this material.



Figure 22: Calcite with fine copper spinel twin crystals on goethite, left under white light, right under SW light, 26-K stope, 1300 level, Cole Mine, specimen - 11cm.



Figure 23: Supergene calcite as crystals to 2.2 cm with copper on goethite, left under white light, right under SW light, Czar Mine, specimen - 6.8cm.

This is true district-wide and the presence of other species, such as cuprite or malachite, does not appear to affect this strong fluorescence. Specimens of copper and calcite from the Campbell, Cole, Czar and Hoatson mines are the most common of this type. The reason for the invariable red – red/orange fluorescence of calcite when elemental copper is present remains unclear. Lead is known to be essential as a co-activator for bright red fluorescence, perhaps it is universally present with elementary copper. Lead is a common, widely distributed element in ore deposits at Bisbee.

Hypogene calcite is widely distributed and is abundant as both localized hypogene alteration of preexisting carbonate rock units, which occurred during mineralization and as hypogene deposited crystals lining hydrothermally developed voids, which appear to be post-mineral, paragenetically. Crystalline hypogene calcite in the western part of the mineralized area is quite rare. It appears to have been either replaced or overgrown by supergene calcite, if not replaced by other secondary

minerals such as siderite or goethite (Graeme, et al. 2016a), as numerous epimorphs of these iron minerals after calcite have been found (see Figure 24 at the left).

However, non-crystalline hypogene calcite, as a product of hydrothermal activity, such as shown in Figures 1 and 2 was widely distributed throughout the whole of the mineralized area. An unusual hydrothermal calcite occurrence in the western part of the district was on the 100 level of the Higgins Mine. Some calcite marine fossils (*Atrypa reticularis*) had been altered and fluoresced a vivid red/orange.

Crystalline hypothermal calcite was reasonably common in the deeper levels of the mines in the eastern part of the district, yet none was noted in the southern portion. Rarely, very small to modest sized openings were found near or in the limestone hosted sulfides near the Sacramento Stock Complex (DeWilde, 1915). While calcite did occur in these openings, amethystine quartz was far more common. An example of calcite from such a pocket is shown below in Figure 25.

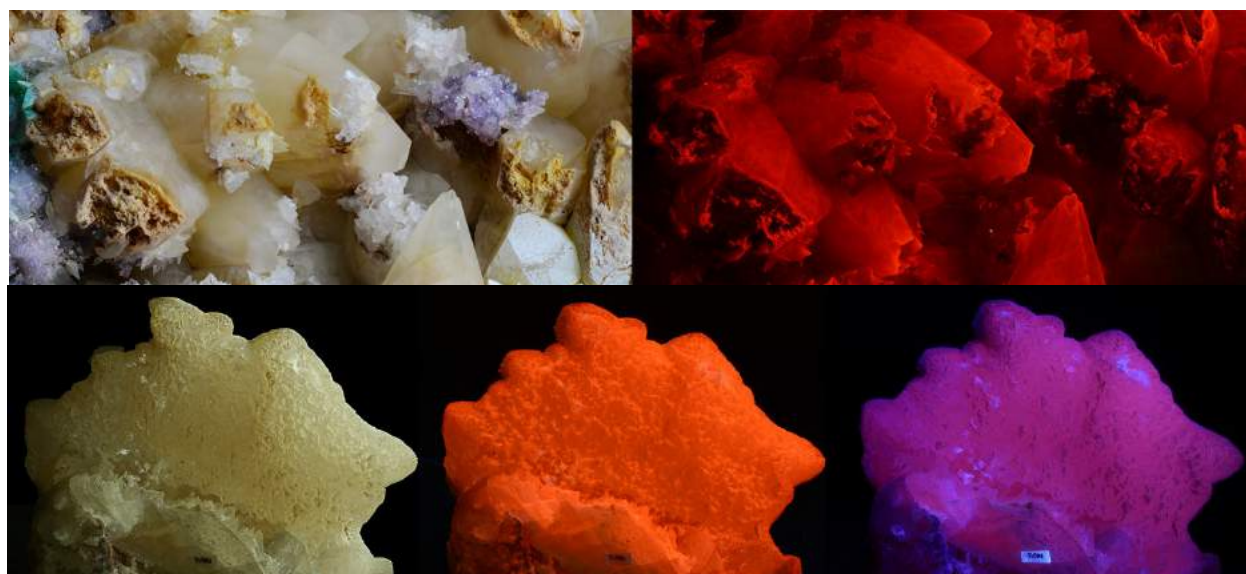


Figure 26: Hydrothermal calcite under white light – left, under SW light – center and under LW light at the right. Specimen 11.4 cm, from the Junction Mine.



A few of the hydrothermal developed pockets in eastern area were large, with several more than 20 meters in overall length, though most were smaller (Graeme, et al., 2016a). Many were completely or at least

Figure 24: (left), Siderite as epimorph-type pseudomorphs after hypogene calcite. Holbrook Extension, Lavender Pit Mine, view - 4.9 cm.

partially crystal lined with hypogene calcite. Most of the hydrothermal calcite exhibited some level of fluorescence, both in SW and LW light, but generally weak. An example of an uncommonly responsive specimen is shown below in Figure 26.

It would appear that almost all of these hydrothermal pockets were formed and were crystal lined after mineralization had occurred, given that but a very few contained any sulfide minerals and without exception, these were quite small and associated with the ores (Figure 25). Many of these calcite crystals show phantoms of included minerals that are invariably iron or manganese oxides.

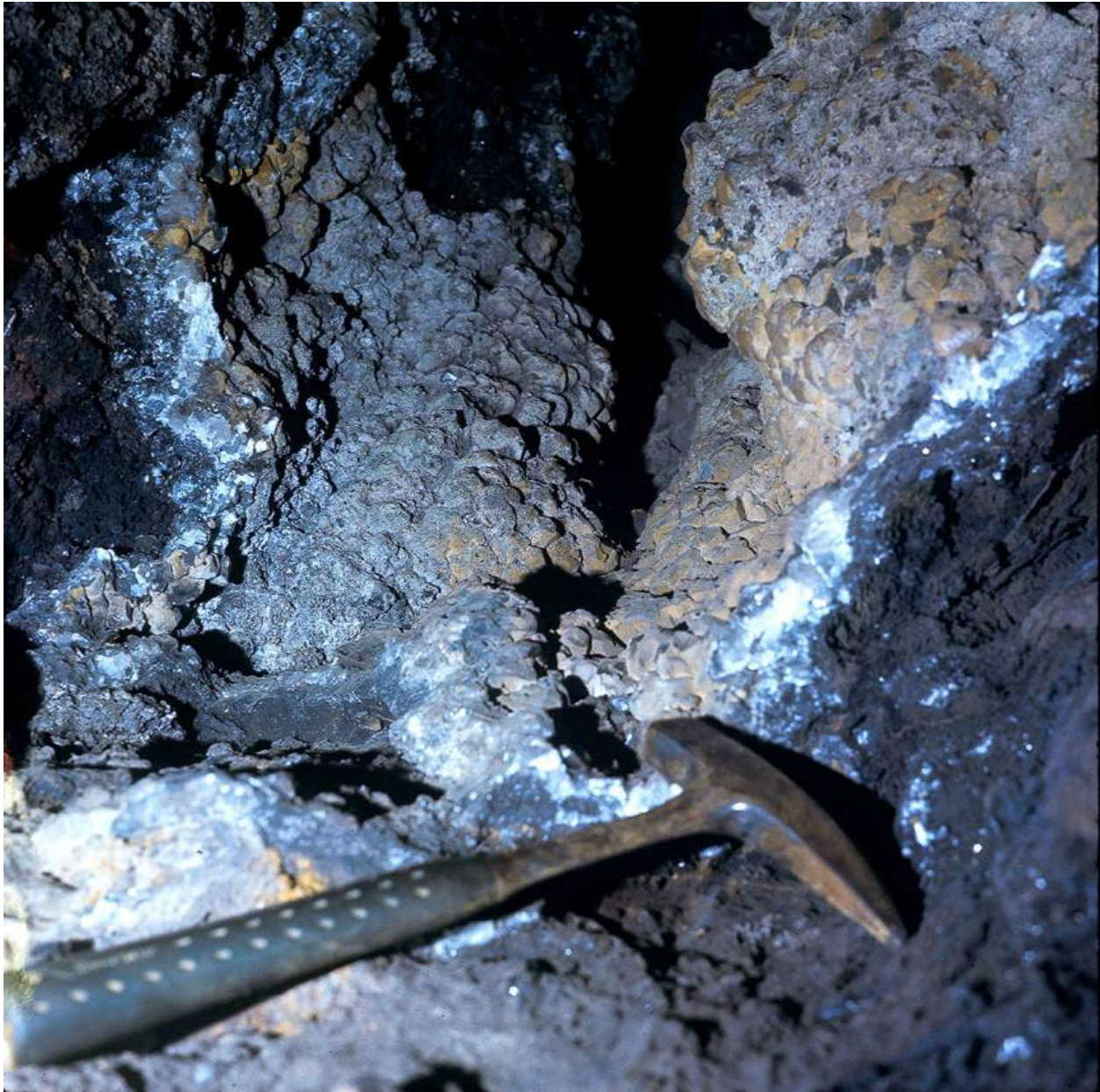


Figure 27: Hypogene calcite in-situ, with a very thin veneer of goethite and on an unidentified manganese oxide, 2700 level, Campbell Mine in 1972. The manganese oxide is probably residual from the dissolving of the altered Martin Limestone by hydrothermal activity.

For the most part, these openings were distant from the orebodies, even from the lead/zinc ores, which, in turn, were distal from the pyrite/copper deposits in the Campbell and Denn mines where



most occurred (Hogue & Wilson, 1950). One of us (RWG III) spent a good deal of time studying and collecting specimens from these pockets during the 1960s as a miner, and then, later in the early 1970s when he was the Resident Geologist at the Copper Queen Branch.

Figure 29: (left), Calcite with minor goethite under SW light, 2566 level, Campbell Mine, Specimen - 6 cm.

Several pockets in the Campbell Mine contained goethite, one as stalactitic forms upon which fine pseudohexagonal calcite crystals were deposited (see Figure, 30), yet there is no sign of sulfides having oxidized to form the goethite, as the surrounding limestone, while somewhat siliceous, appeared fresh and clean; totally free of sulfides or oxidation features. Even the typical casts of removed pyrite and staining caused by mobilization of iron were both absent in the encasing limestone. And too, the depth of more than 750 meters, is such that supergene oxidation is largely precluded.

Thin films or even crust of late-stage goethite often coat some of the calcite crystals, but in general there is no evidence of corrosion that typically accompanies even the slightest of coatings of carbonate minerals by goethite in supergene environments (see Figure 23). However, some very localized hydrothermal exsolution of calcite has been recognized in a few small pockets in or near sulfides, as can be seen in Figure 25.



Even though some of the crystalline hypogene calcite does not fluoresce, when identified manganese oxide under SW light, 2566

it does, it can be spectacular. The examples presented herein are but a very few examples of the more common types which a collector is likely to own.



Figure 30: Hydrothermal calcite which has overgrown goethite stalactites and is partially coated by later goethite, which in turn, is partially overgrown by a later generation of white to colorless, hydrothermal calcite. Under SW light, from the 2566 level Campbell Mine, Specimen – 8.2 cm.

The primary locality for highly fluorescent material at Bisbee has to be the hydrothermal calcite from the 2566 level of the Campbell Mine, such as shown in Figure 30. While several locations on and above this level produced fine examples, as shown above, one site was outstanding. Calcite occurs as a coating of goethite on pseudohexagonal crystals to 1.5 cm and typically has a second-generation calcite overgrowth that yields a bright red fluorescence under SW light, but a much more muted one to LW. The earlier, coated calcite is somewhat fluorescent as well, but this is usually obscured, at least in part, by the near-pervasive goethite coating and the brilliance of the later calcite. An unusual example of an un-coated specimen is in Figure 31 below.

Hundreds of specimens of this type of calcite were recovered in the late 1940s, during lead/zinc mining. Unfortunately, few of the specimens collected survived the often-careless collecting or poor handling during removal, without significant damage. The incredibly hard matrix rock did much to make collecting difficult and the lack of desirability of calcite as mineral specimens at the time, caused them to be roughly handled. As a result, only a modest number of the hundreds collected are significantly free of damage to make collector quality specimens today, but their brilliant and contrasting fluorescence still remains.



Figure 31: Hydrothermal calcite under SW light from the same location as that in Figure 30, but lacking the typical goethite coating and late stage partial calcite overgrowth, specimen – 6 cm.

Several other pockets of hydrothermal calcite in the Campbell also produced highly fluorescent specimens, often in complex crystal forms. These were also found during the late 1940s to the early 1950s, but are far fewer in number and even fewer specimens were preserved. It was, after all, just “calcite,” reflecting a continuing deep under appreciation of this enchanting mineral.

Nonetheless, among the surviving specimens, some of the complex, colorless to white crystals give a most pleasing pinkish-orange or even a salmon color under SW. Little to no LW response has been observed. Interesting and large (8 – 20 cm.) cream-colored scalenohedrons from a hydrothermally enlarged fault, well east of the shaft on the 2200 level fluoresce a muted white.

These latter scalenohedrons were often coated by amethystine quartz, masking their underlying fluorescence.

Cerussite: Cerussite was a common ore mineral in the western, oxidized part of the district. Some orebodies containing several tens of thousands of tons of cerussite, almost always as massive, spongy/boxwork to a sandy material. It was also abundant as crystalline material mixed with and/or on malachite or azurite. Small (one cm.) sixling-twin crystals on coronadite were common in the mid-levels of the Campbell Mine. Fortunately, a number of small, but handsome Bisbee cerussite specimens can be found in numerous collections.

However, fluorescent cerussite appears to be quite uncommon, if not rare. More than two dozen Bisbee cerussite specimens in our collection were checked for fluorescence under both SW and LW, but only one, that illustrated below, responded to UV light, with a near-white color under SW and a very muted rose color under LW. This may well suggest the presence of a mixture or an extraneous element in this single specimen.

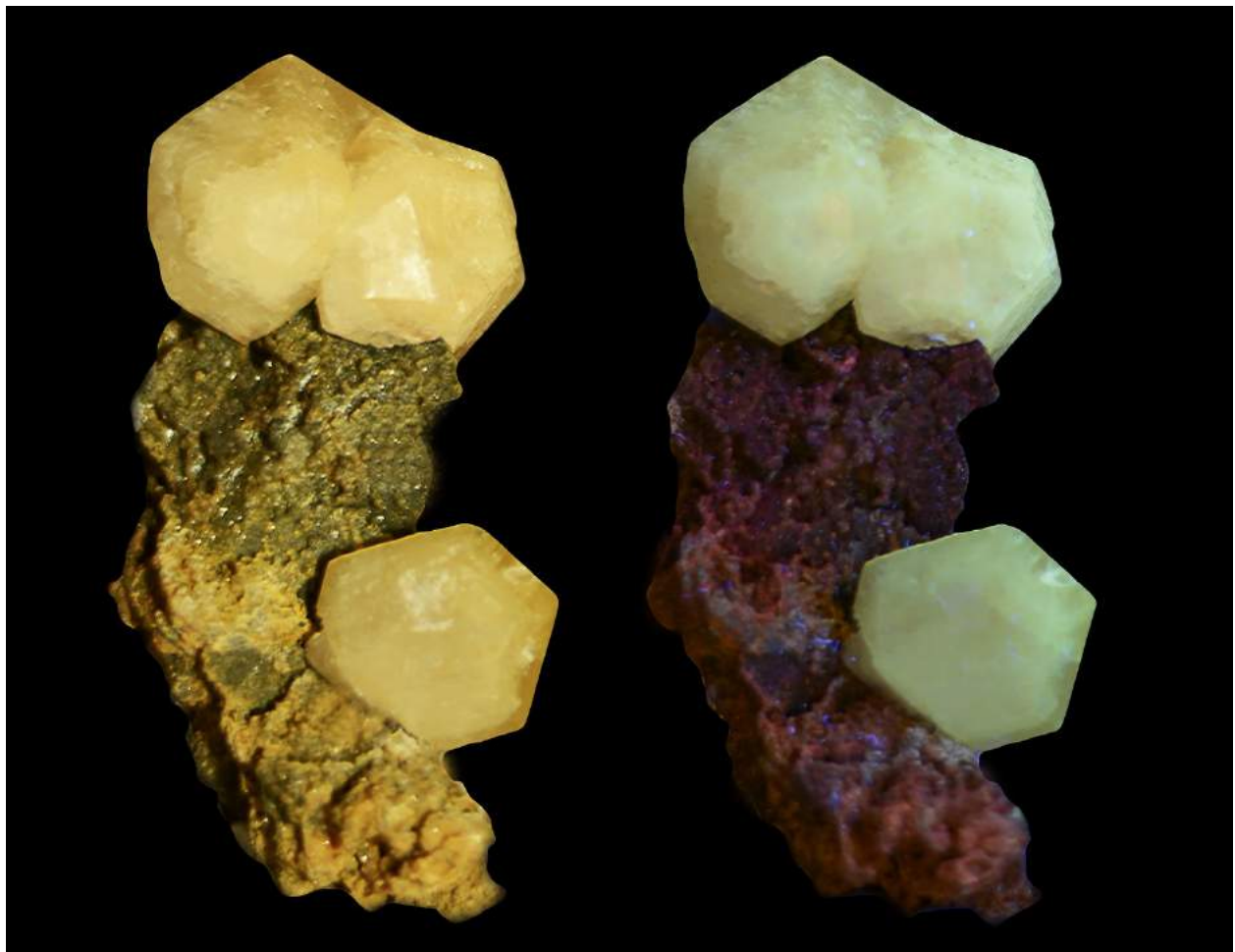


Figure 32: Cerussite on smithsonite and goethite under SW light (right), Gardner Mine, specimen - 7.1 cm.

Dolomite: Dolomite was common throughout the District as a rock forming mineral within the Martin limestone. While often manganese enriched, as previously noted, no fluorescence has been observed in the rock unit by the authors in our numerous test underground.

Dolomite was also relatively common as a minor supergene mineral in many of the oxidation caves, typically as a late-forming deposit, partially coating calcite and/or aragonite, some of which will fluoresce a white to cream color under both SW and LW light. However, in general, supergene dolomite was rarely fluorescent, even mildly.



Figure 33: White to cream colored fluorescing dolomite on superb, light-blue fluorescing aragonite crystals to 3.5 cm, under SW light 7^h level, Southwest Mine.

Fluorite: The most typical mode of occurrence is as a minor accessory mineral in the intrusive units, particularly the Juniper Flat granite where it is found as veins, blebs, and bunches of massive, deep purple material that fluoresces a light green. The several other fluorite localities in the district yield material which fluoresces a very weak white/yellow under SW.

Gypsum: Supergene gypsum was most common in a number of the oxidation caves, but never abundant. It occurred as the classic rams-horn growths and coatings over calcite and in the one case as feather-light blocks of small, thin crystals as shown in Figure 34.

Fluorescent gypsum has been noted on just two of the many caves. This probably does not truly reflect the actual distribution, because access to these caves is often impossible, as the ground has caved and/or they were backfilled for safety reasons. And too, gypsum at Bisbee was uninspiring at best, thus very little was collected. Thus, fluorescent gypsum may well have been more common than represented herein.

Several oxidation caves in the Southwest and Shattuck mines contained gypsum that formed as a coating or growths on a calcite base, which is equally bright green in fluorescence.

Post-mining gypsum as the crystalline variety selenite was common in oxidizing sulfide zones (Graeme, et al., 2016b), but was never found to be fluorescent.



Figure 34: Partially fluorescent gypsum under SW light, with very minor flecks of included malachite 6th level, Southwest Mine, specimen - 9 cm.

Hemimorphite: Hemimorphite was one of the few common supergene silicate minerals at Bisbee, but very, little was fluorescent and that was under SW light only. A limited number of specimens from Cole and the Copper Queen mines exhibit partial fluorescence. The many specimens checked from other mines and even others from the Cole and Copper Queen mines did not fluoresce.

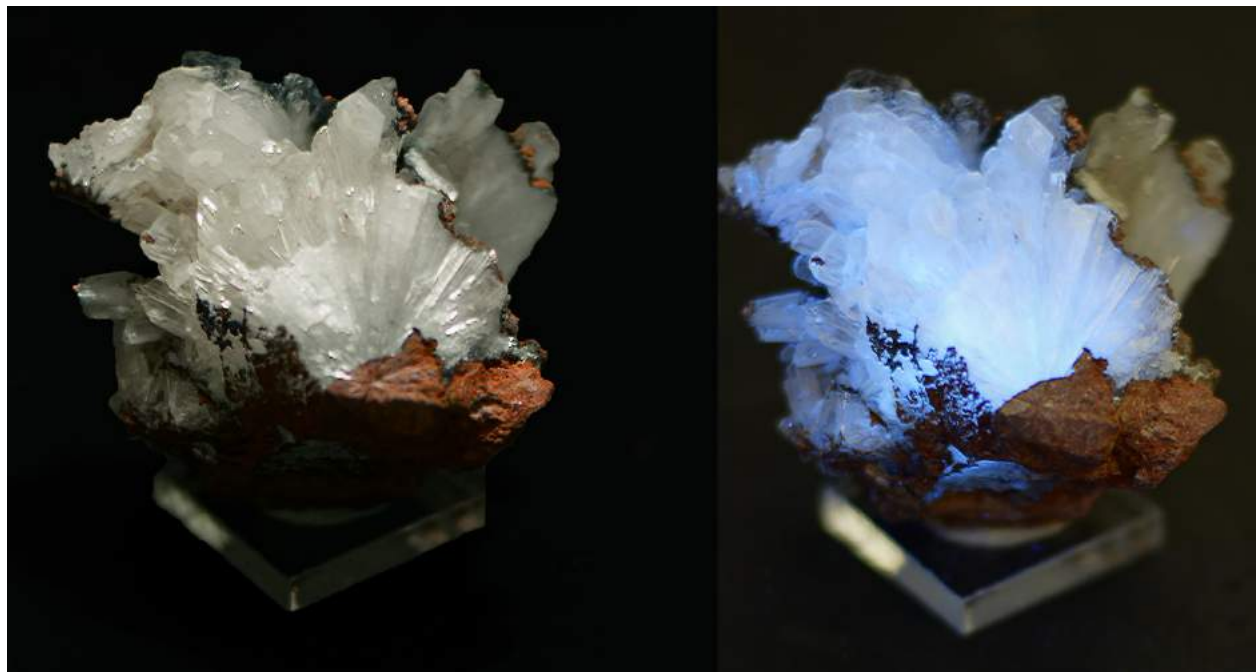


Figure 35: Bright-white partial fluorescing hemimorphite on hematite with Chalcophanite under SW light, 26 K stope, 1200 level, Cole Mine, specimen – 3.6 cm.

Hydrozincite: Hydrozincite, a common fluorescent mineral, has been noted in modest amounts in a number of localities throughout the oxidized ores. For the most part, hydrozincite was found as scattered, localized coatings with other oxide minerals in/on partially oxidized sphalerite.

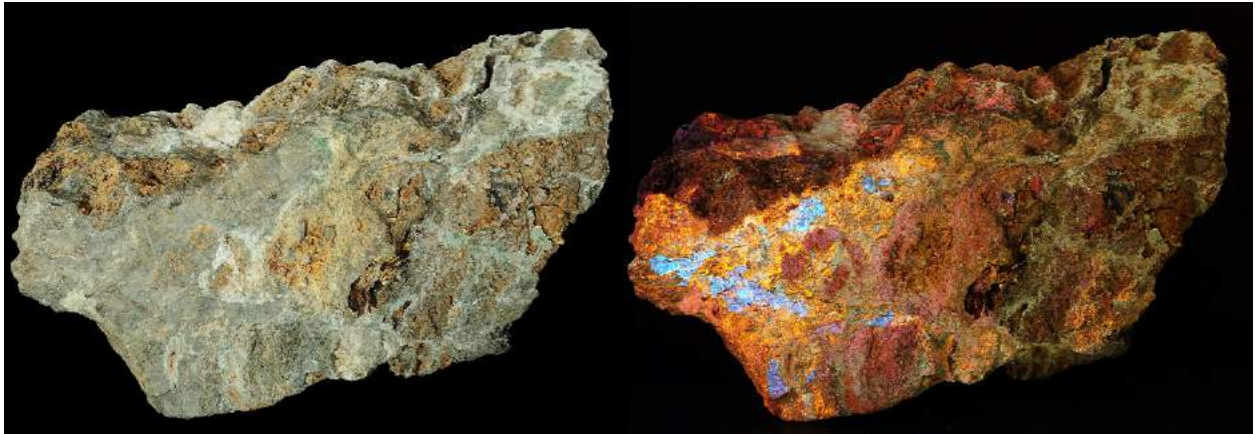


Figure 36: Hydrozincite fluorescing the typical blue-white color. It is associated with sphalerite (orange fluorescence), calcite as both fluorescent (red) and non-fluorescent material, such as smithsonite and goethite - under SW light. The specimen is relatively large at 15.4 kg and 33 cm in length. It is from the B level of the Copper Queen Mine at the location shown in Figure 37.



Figure 37: Blue to blue-white fluorescing, post-mining hydrozincite on orange fluorescing sphalerite with red fluorescing calcite illuminated by SW light, except where the person is seated, which was painted with white light, B Level, Copper Queen Mine. The photo is a merged panorama of two images to include the left side, with the person in the same place, in both. No other photo editing applications used.

In the transition zones, those areas where the sulfide minerals were undergoing oxidation, hydrozincite often was associated with the remaining sphalerite. An example of this type of occurrence is shown here in Figure 36.

Post-mining hydrozincite was common where ever sphalerite had been exposed by mining and left in place (Graeme et al., 2016b). It was not uncommon for isolated pods of sphalerite to be found during mining and bypassed, some of which contained thousands of tons. This was, after all, a copper mine with no zinc recovery facility. One such area found during the 1880s is shown in Figure 37 at the left.

Opal: Opal has been found in several areas in the mines as a late-stage mineral. Common variety opal occurred in the western part of the district, particularly the Southwest mine area, where it was moderately abundant as a tan to brownish to gray material up to a centimeter thick. Under SW ultraviolet light, most of this opal was green in fluorescence, while some was cream-colored.

Along the fringes of a large collapsed stope above the 100 level of the Higgins Mine level were pockets of calcite, several of which had spotty, partial coatings of highly fluorescent under SW hyalite opal, as thin, patchy coatings on the tips of goethite stalactites with calcite. These pockets were in limestone that graded into massive supergene hematite/goethite.

Powellite: Powellite is a mineral of apparent limited distribution in the district. Powellite has been reported from several locations, but only one occurrence can be confirmed in small amounts at the Bisbee Queen Mine, an exploration shaft on the eastern side of the district Anthony, et al. (1995).

Quartz: Chalcedonic quartz is widely distributed within the district, mostly associated with the Cretaceous sediments. Little of this material is fluorescent, except for that near the Easter Sunday Mine on the eastern fringe of the district. This chalcedony yields a light green color with zones of darker green in the same specimen under SW light.

Scheelite: Modest amounts of scheelite associated with quartz, minor chalcocite and tiny amounts of cuprotungstite were found in a small deposit in Cretaceous age sediments on the eastern edge of the district. As is so typical, the scheelite is strongly fluorescent, yielding the typical bright blue-white response under SW light. However, it does not respond to LW light.

Scheelite was also widely distributed in the sulfide ores in tiny amounts as a minor accessory mineral, associated with wide range of rare or unusual copper, lead, zinc, gold, silver, tin vanadium, arsenic, bismuth and antimony bearing species (Schumer, 2017).

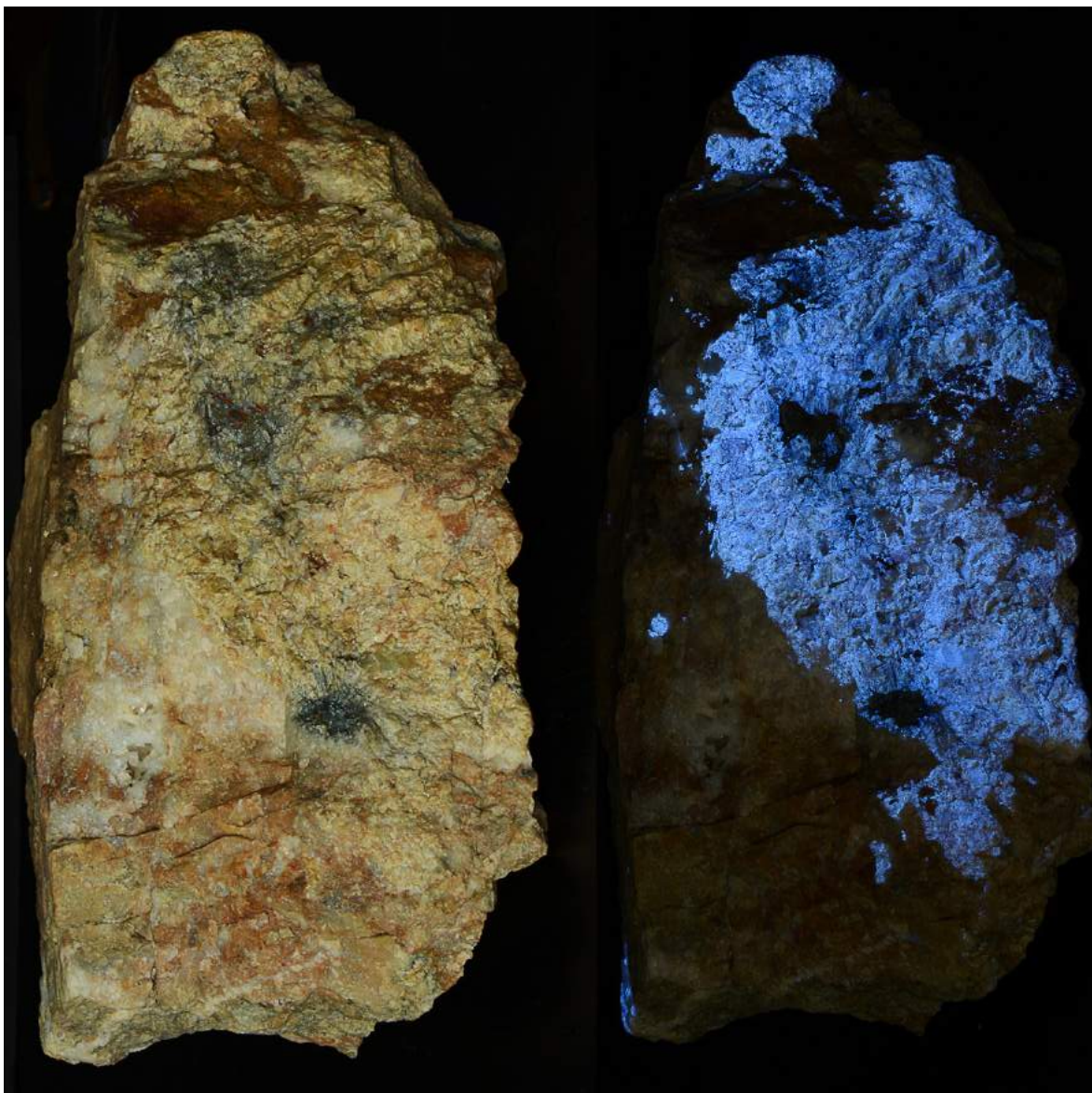


Figure 38: Blue-white fluorescing scheelite on quartz with minor black chalcocite under SW light, from near the Portage Lake Mine, specimen – 20 cm.

Sphalerite: Millions of tons of sphalerite were mined at Bisbee, but very little was fluorescent, or perhaps better said, recognized as fluorescent. Miners did occasionally note triboluminescent sphalerite, as it sparked and briefly glowed when struck with steel tools. Some color variation has been noted in fluorescent sphalerite, but far and away, orange is the dominate response.

The Junction mine produced compact, fine-grained, iron-rich sphalerite that gave a bright orange response to SW. Only a relatively small number of these otherwise nondescript specimens were saved. Examples from three separate and distant occurrences in this huge mine are presented below under SW light. Interestingly, these and other sphalerite specimens from these mines responded weakly if at all to LW.

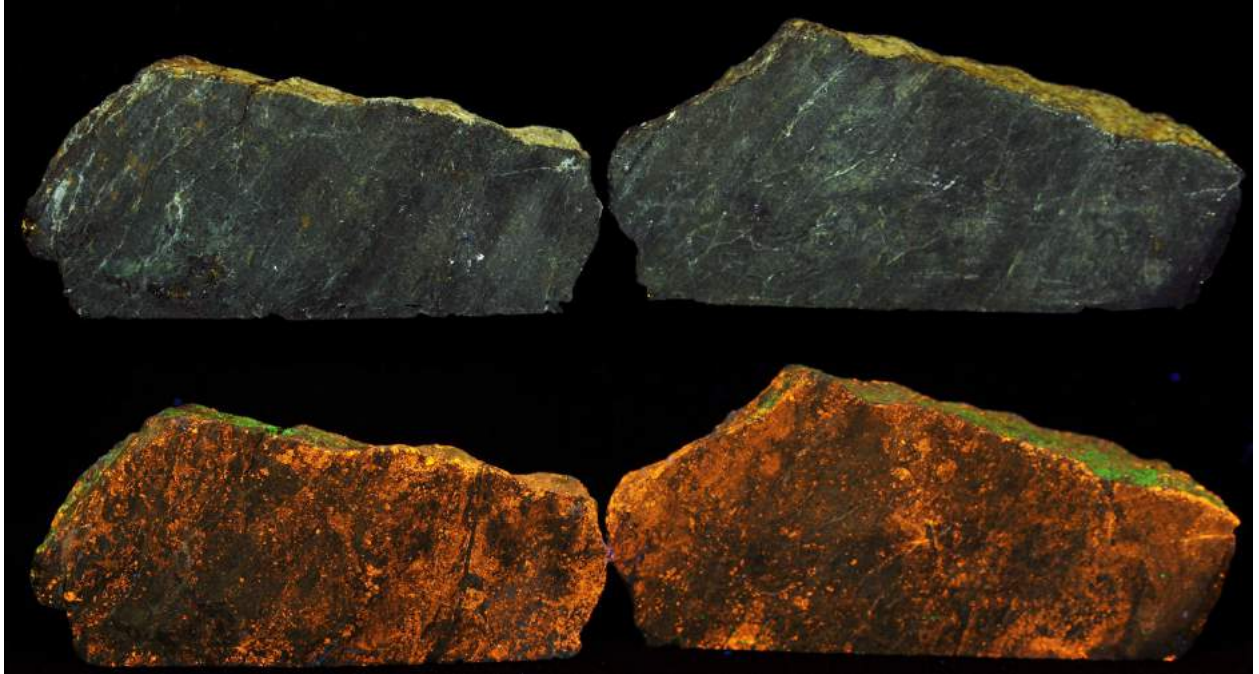


Figure 39: Extremely fine-grained mass of sphalerite, which has been cut and polished for study under SW light. The near-parallel orientation of the sphalerite many well relic textures of the replaced limestone. Junction Mine, specimens - 5.5 cm.



Figure 40: Sphalerite fluorescing a yellow/orange hue under SW light. Note the pyrite present at the top left. Specimen from the Junction Mine, size – 4 cm.



Figure 41: Sphalerite under SW light, Junction Mine, specimen - 9 cm.

A small pod of partially oxidized sphalerite above the “B” level of the Copper Queen Mine contained some of the most vividly fluorescent sphalerite under both SW and LW light ever noted by us at Bisbee.

It was associated with equally fluorescent calcite and minor post-mining hydrozincite, as shown in Figure 36. The sphalerite was left in place because a zinc recovery system did not exist in the 1880s when it was found. Also, the small size of the sphalerite deposit would not justify the cost and effort to mine and recover the contained zinc.

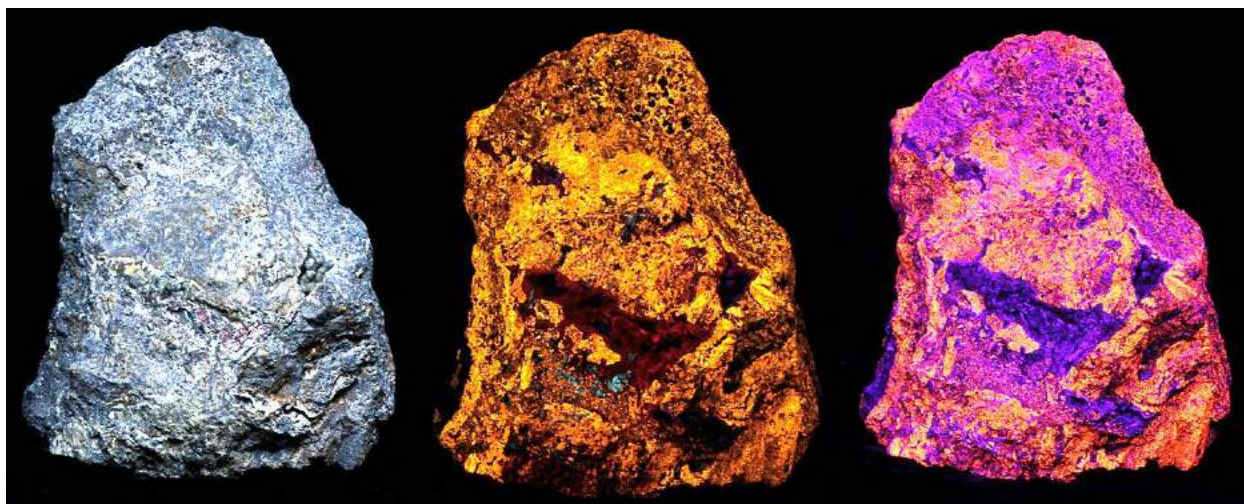


Figure 42: Sphalerite, with minor calcite and smithsonite. Left - under white light, center - under SW light, right - under LW light, B level, Copper Queen Mine, specimen – 9 cm.

Uranopilite: Uranium minerals were not uncommon in small amounts at Bisbee, but seldom recognized and less often recovered. They too suffered from the near-myopic focus of the Bisbee collecting community on the vividly colored copper carbonates, so few were collected.

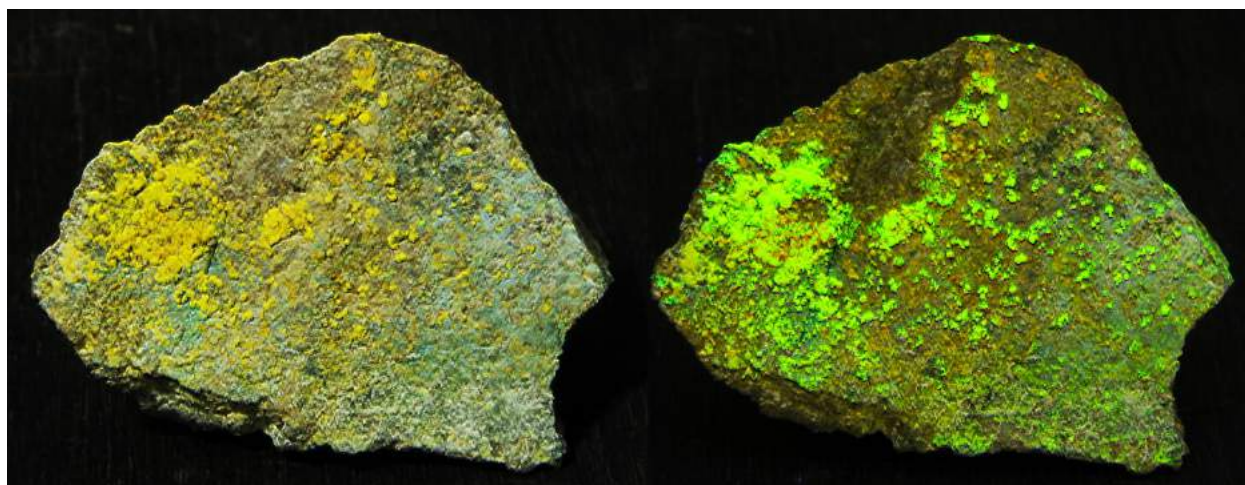


Figure 43: Uranopilite with minor zippeite on pyritic limestone under SW light, Cole Mine, specimen – 4.5 cm.

Willemite: This common zinc mineral has been recognized in several scattered localities within the district, all of which produced highly fluorescent material under SW light (Anthony, et al., 1995, Graeme, et al. 2015). Indeed, it was largely the fluorescence that caused willemite to be recognized. A vivid green response under short-wave ultraviolet light is given by all of the willemite recognized in the district. However, no response to LW light has been noted in the specimens examined.

The abundant willemite found in the Cuprite Stope on the Tunnel level of the Higgins mine is also strongly phosphorescent. This material is the only phosphorescent material recognized during this

study. After the SW light source is removed, the willemite will continue to glow strongly, slowly diminishing until completion extinction, some 20+ seconds later.

During the late 1940s, highly fluorescent willemite was recognized with lead/zinc ores in the Campbell Mine. Several miners collected the material to sell to the mineral dealers who frequently passed through Bisbee (Melvin Elkins, personal communication, 2016). Local demand for fluorescent material was limited to nil, as Bisbee collectors had little interest in such specimens.

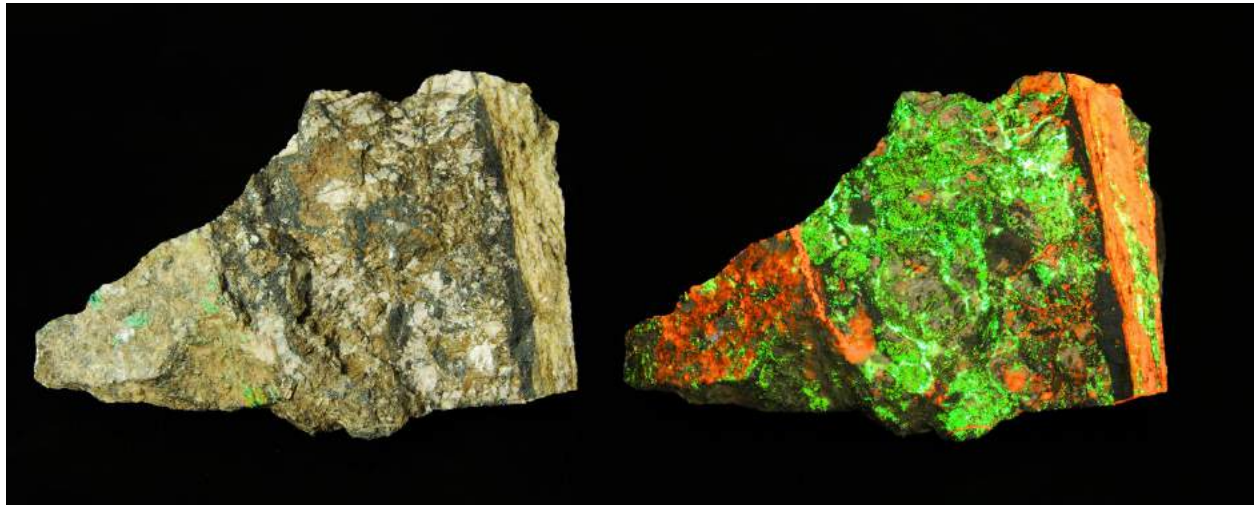


Figure 44: Willemite fluorescing the typical bright green color. It is associated with minor nonfluorescent malachite and highly fluorescent calcite (red, red/orange fluorescence). Under white light, left and under SW light, right. Cuprite stope, Tunnel level, Higgins Mine, specimen – 11.5 cm.

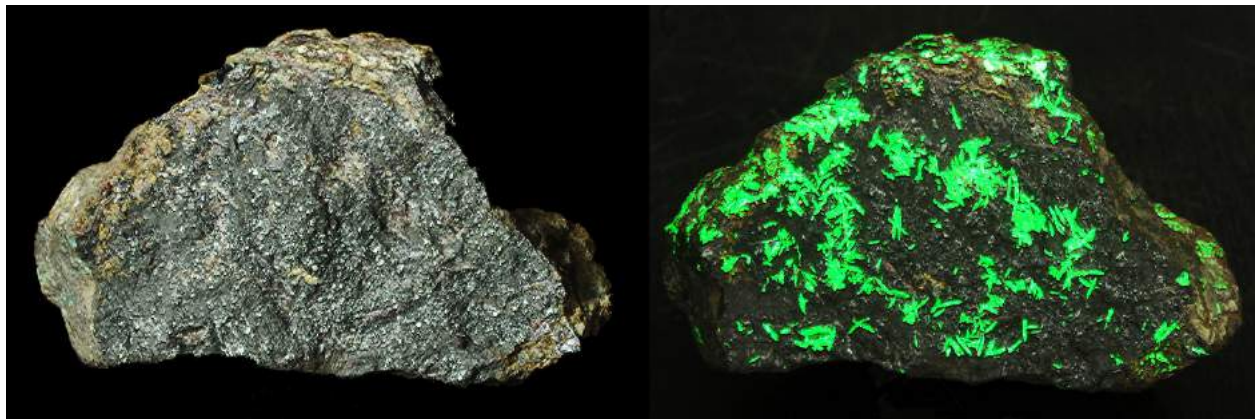


Figure 45: Colorless willemite crystals to 2 mm. on braunite under white light, left and under SW light right, Cuprite stope, Tunnel level, Higgins Mine.

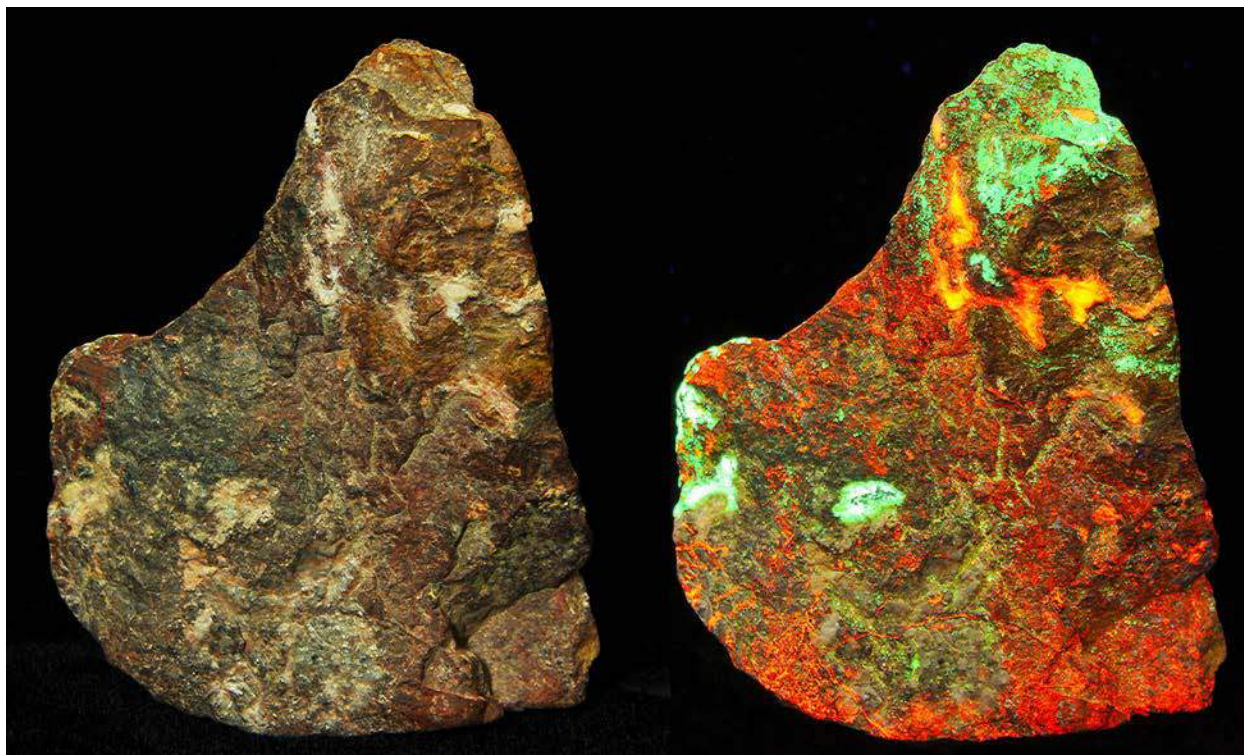


Figure 46: Willemite (green) with highly fluorescent, iron-stained calcite (red – re/orange); Left under white light, right under SW light, 2100 level, Campbell Mine, specimen – 11 cm.

SUMMARY

Fluorescence is an important part of mineralogy, both in the hobby and the science. With the hobby, fluorescence brings additional enjoyment with this added dimension along with a better understanding of the minerals present.

For the science, it is an absolutely essential tool in the study of most any specimen and deposit. No specimen passes through our laboratory without at least a quick check for fluorescence. More than once we have been surprised by fluorescence, sometimes just as a speck.

Fluorescence has played an important role in our decades-long study of Bisbee and its minerals. Several species new to the district have been recognized by fluorescence or their association with fluorescent minerals, which otherwise may have gone unrecognized. New localities for fluorescent species in the district have been found, as noted in this paper. And too, using fluorescence to study the physical characteristics of fluorescent minerals by the often-variable nature of fluorescence in specimens has been instructive, as shown in Figure 47 below.



Figure 47: Using SW light to aid in viewing the orientation and nature of calcite crystals and fragments in recrystallized, calcite cementing a limestone breccia. This is the same specimen presented as Figure 1: No effort was made to assure color correctness, but rather contrast was sought to mark crystal/fragment boundaries. View – 5.5 cm, 3 level Southwest Mine.

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