THE MINERALOGY OF BISBEE, ARIZONA

THE GEOLOGY AND MINERALOGY

VOLUME 1

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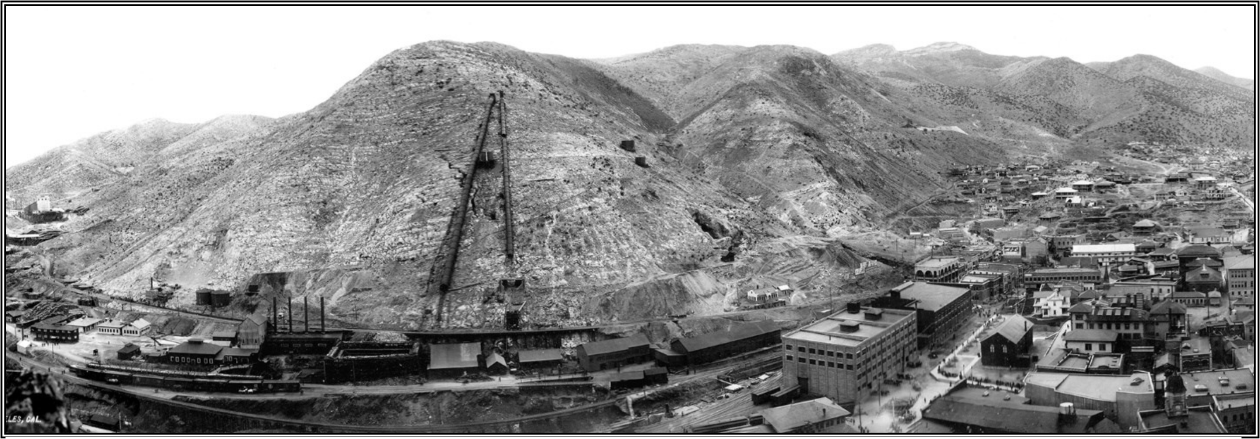
Layout by the authors

Front cover: Azurite on malachite Holbrook Mine, specimen-11 cm. Graeme collection.

Back cover: Cuprite nodules to be broken; 14 stope, 5th level Southwest Mine.



Bisbee, Arizona Territory, looking south – 1909. The great Czar mine is at the lower center left.

Bisbee, Arizona, looking south – 2019. The Queen Mine Tours is at the lower center.

BISBEE, ARIZONA 110 YEARS APART

In 1909, Bisbee was very much an industrial town with more than 25,000 souls earning a good living working in the mines, mine shops and the many private commercial enterprises that provided for the needs of a very active and expanding community. By the time this photograph was taken, the ore deposits had been found to extend for more than a mile to the east and to the south and to a much greater depth than ever imagined. A long and prosperous future was assured and indeed, enjoyed, to the great benefit of all.

In most ways, Bisbee was very much like other western mining towns of the era, except that it had a future. With this future came substantial investment by the owners of the various mines to invest in the development of the community and take a long-term view of the workers wellbeing to develop a stable workforce. The best wages of any mine anywhere were paid and the working conditions and safety were unmatched anywhere.

By 2019, the mines had been inactive for 44 years. Today, the small charming town is home to less than 6,000 persons and tourism is the main business. Because Bisbee has retained much its early 19th century character, it has a future sharing the enchanting feeling of a time long-ago with tourist for so long as we have a curiosity of the past.

The three volumes of this set bring forth the often-unseen wonders that set Bisbee apart as a geologic marvel with a mineral legacy that is unmatched in the United States and an inside look at how Bisbee became the renouned jewel that it is.

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FORWARD

This work represents over 70 years of studying this incredible deposit and all of the minerals that occurred therein. During these years, we have had the unparalleled opportunity to walk through hundreds of miles of the mine workings and visit most of the localities recorded herein, beginning in 1948. Coupled with these thousands of hours of underground fieldwork was the opportunity to discuss a wide variety of aspects of the deposit with many who worked in these mines from the beginning until the end, including our grandfather/great-grandfather, who came to Bisbee as a miner in 1883.

This effort could not even have been undertaken, much less completed, without this assistance and wise counsel of a host of individuals. Miners, collectors, geologists, and mining engineers, too numerous to remember much less name, and all with love for Bisbee's minerals, passed on information and often recounted their experiences and observations. Personal communications, which are the most ephemeral and transitory form of information, are often the basis for much of the mineral occurrences recorded, many of which we were able to confirm in the field.

Museums throughout the U.S. and Europe that contain Bisbee minerals in their collections have generously allowed us to review the specimens held therein. Countless collectors have kindly permitted us to study the priceless Bisbee treasures they have had the good fortune to acquire. For these innumerable courtesies, we are very much indebted and grateful.

Our heartfelt thanks go to the great Arizona mineralogist/author/collector and friend for almost 50 years, Richard Bideaux. Dick spent weeks reviewing, editing, and thereby vastly improving the detailed mineralogy part of the manuscript, which forms Volume II, just before his untimely death in October 2004. Oftentimes, just "thank you" is not enough to fully express gratitude; this is one of those occasions. Thus, we dedicate this work to Richard Bideaux in thanks for not only what he did for us in helping with this work, but for what he did for all of us who love minerals. Thank you, Richard Bideaux; it was an honor to know you for several decades.

Dr. Carl A. Francis, formally curator of minerals at Harvard University, has assumed the enormous task of reviewing what Dick Bideaux had completed, with an emphasis on the changes in mineral nomenclature and classification that have taken place over ensuing years. Further, he has brought his keen, knowledgeable eye to reviewing the geology and history, which are contained in their separate volumes. The degree of wisdom he has brought to improve these volumes is outstanding.

Dr. Peter Williams, then Professor Emeritus of the School of Science at Western Sidney University, shared his love and knowledge of cuprite and other related copper minerals. With his help and guidance, the depositional features and chemistry of supergene copper minerals are presented in some detail.

There is a considerable amount of available literature to augment our observations. A thorough and careful review of this information has been made as well in an effort to be as complete and correct as possible. Yet, species new to the district and known species from new localities within the district continue to be found. Thus, this effort must be considered as little more than a baseline for the wealth of information that is yet to come from further and closer examination of the specimens recovered from the many mines at Bisbee. No doubt, more minerals will be discovered, including species new to science. To be sure, advances in the science of mineralogy, both in understanding and determinative technology, will add immensely to the understanding of this, one of the world's finest and most prolific mineral localities.

The illustrations in this study are noted by the source, and some have been cropped to reflect the purpose of use. Photographs included are largely by the authors except as credited. Also, unless noted otherwise, the specimens illustrated are or were in the collection of the authors at the time they were photographed. Likewise, the historical photographs used herein are from the Graeme/Larkin collection, unless otherwise credited.

INTRODUCTION

This work in three volumes is the first and only comprehensive study of the mineralogy of Bisbee, which is, in our very biased opinion, America's finest mineral locality. The volumes are:

The Mineralogy of Bisbee, Arizona
I: Geology and mineralogy

The Mineralogy of Bisbee
II: Detailed Mineralogy

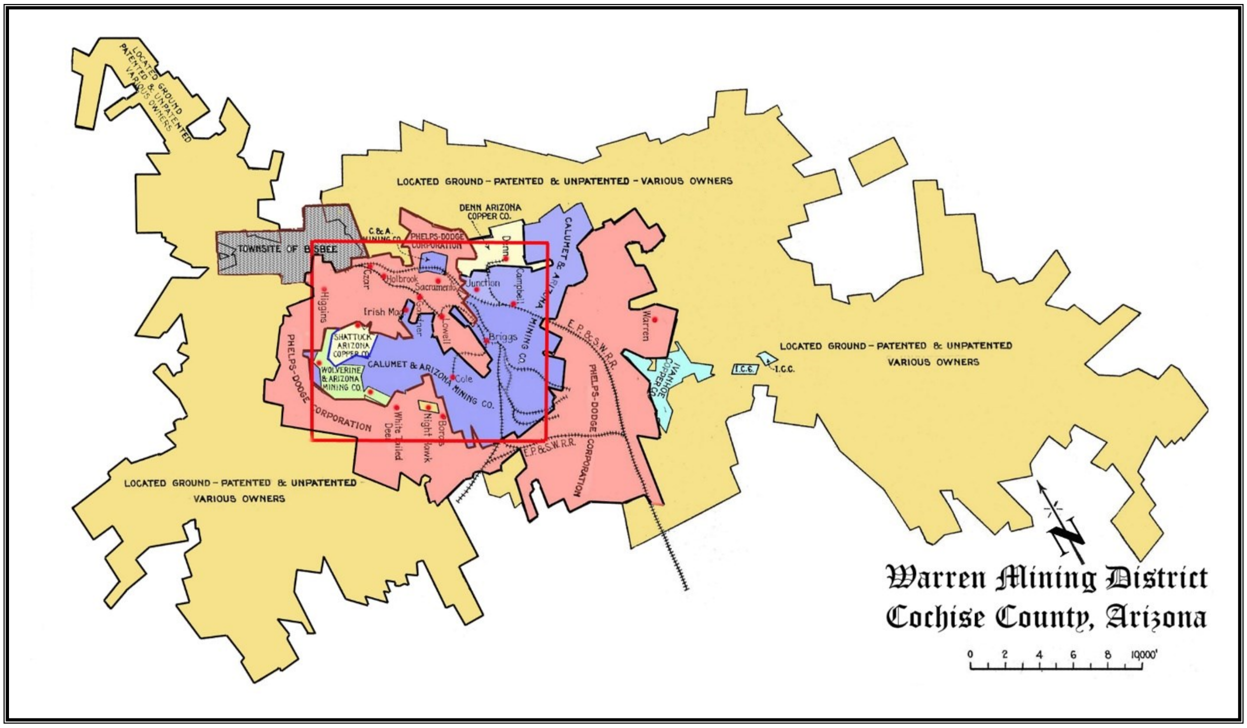
The Mineralogy of Bisbee, Arizona
III: A history of Bisbee as related
to its discovery, mineral collecting
and mineralogical studies.

The many hundreds of carbonate replacement deposits, along with the porphyry hosted copper deposit of the Sacramento Stock Complex at Bisbee, Arizona, were mined for almost a century and were, by any standard, world-class. In all, nearly 8 billion pounds of copper, 355 million pounds of zinc, 324 million pounds of lead, 11 million pounds of manganese, 100 million ounces of silver, and 2.7 million ounces of gold were produced by Bisbee's mines (Graeme, 1981). Yet, despite the immense wealth that came from these metals, it was the spectacular minerals that made Bisbee famous long before the extent or richness of the ore deposits were ever realized. Even now, these 45 plus years after the last mining stopped, it is the legacy of Bisbee's minerals that ensures its continued fame.

These unique deposits have been the source of a large number of beautiful specimens and have also produced a surprisingly large number of mineral species. As of this writing (December 2020), more than 337 distinct mineral species have been recognized as coming from Bisbee. Clearly, more are yet to be discovered in the massive number of specimens that were saved during mining and are preserved in public and private collections today.

Over the years, numerous studies of Bisbee's ores were made, yet no definitive study has ever been undertaken of the minerals and their depositional environment. The complexity of the many scattered sulfide, carbonate-hosted replacement deposits, their complex mineralogy, and the various supergene episodes; precluded such a study without a commitment of decades of work and substantial resources for determinations and countless lab tests as well as in travel to see collections, locate and review the pertinent literature, and much more. An unparalleled resource, represented by our 7,000 plus Bisbee specimen library, which is mainly self-collected, yielded so much information about the context of the minerals as well as the ability to review the interpretive information in our own expansive library of books, reports, and maps. No other such collection is known to exist or has ever existed. Further, we do not believe a similar collection could be developed in the future because of the enormous self-collected component gathered over the last 70 years.

One of the first challenges faced in undertaking this work was to define "Bisbee" from a mineral occurrence perspective. A clear option was to focus only on the economically important area and the minerals associated with the ore deposits and their host rocks. Much of the available literature was, understandably, devoted to this sector. This approach would have excluded some essential areas such as the genetically related, but, until recently, uneconomic copper mineralization just north of the Dividend fault.

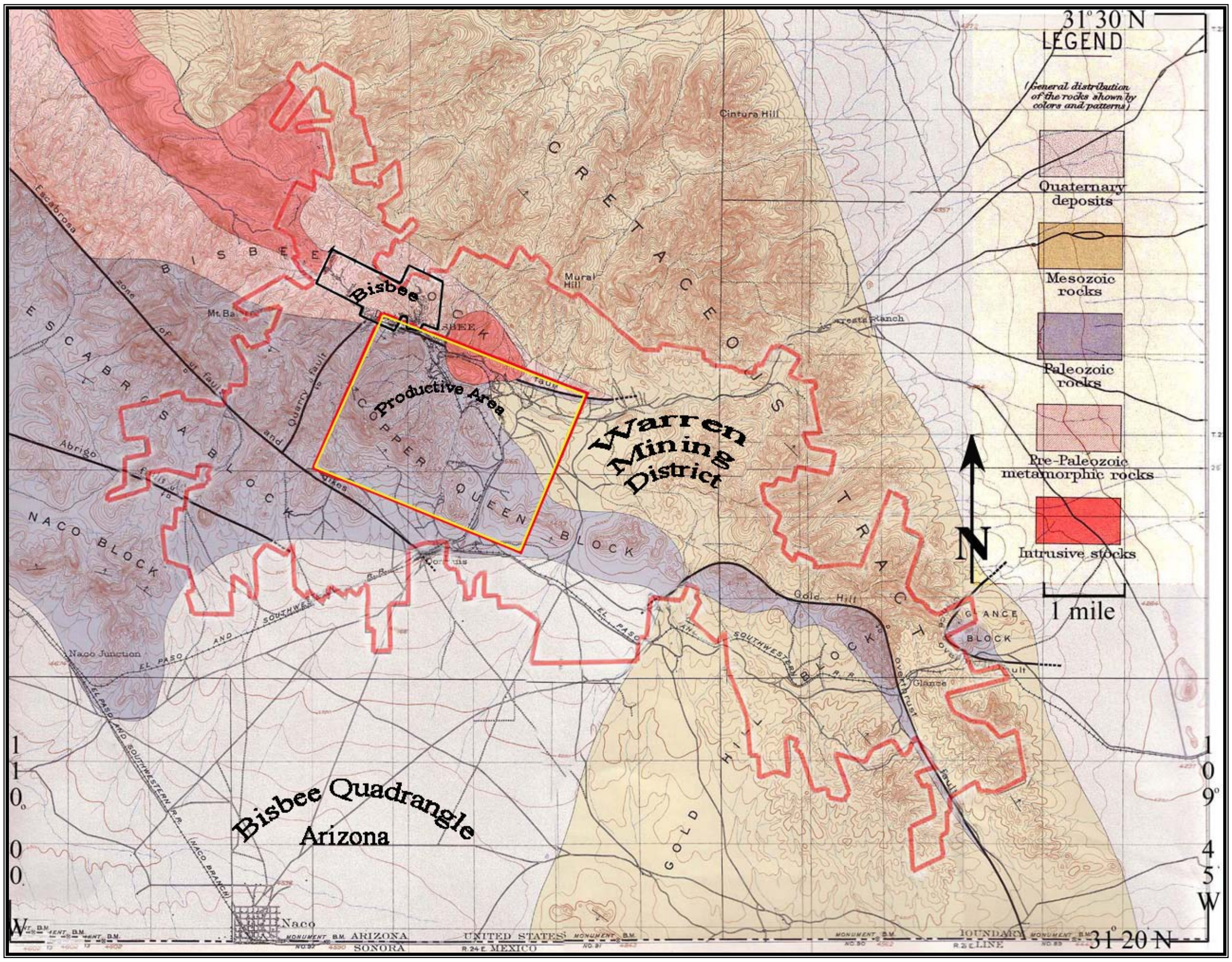


The Warren Mining District in 1922, with the productive area outlined in red, after Elsing, et al. (1922).

Then there was the possibility of restricting the study to the Warren Mining District. This much larger area includes all of the ore deposits as well as a substantial amount of the surrounding area. Ricketts (1943) defined a mining district as *"A section of country usually designated by name, having described or understood boundaries within which minerals are found and worked under rules and regulations prescribed by the miners therein. There is no limit to its territorial extent and its boundaries may be changed if vested rights are not thereby interfered with."* However, this approach would ignore the nearby Juniper Flat area, with modest but interesting mineralization that is probably related to that of the economic zone.

In the end, it seemed most reasonable to take the approach first developed by Fredrick Ransome in his classic 1904 geologic study of the Bisbee area and use the quadrangle as it was defined in this work. *"It is inclosed* [sic] *by meridians 109º 45' and 110º and parallels 31º 30′ and 31º 20′, the latter being locally the Mexican boundary line."* (Ransome, 1904a).

This approach fully encompassed the areas with all of the related intrusive and mineralizing events and the areas to the east with their later mineralization. However, the term "district" has been frequently employed, reflecting its historical usage and further defining localities as occurring within the mining district as opposed to outside of this designated area.



General Geology of the Bisbee Quadrangle, with outlines of the Warren Mining District and the productive area. After Ransome, 1904.

GEOLOGY

Sacrament Hill-1904-looking east

A wealth of geologic and historical information can be found in this overview of Sacramento Hill (Sac Hill). The several intrusive units that compose the Sacramento Stock Complex as well as the associated hydrothermal alteration that rings it, and which has been deeply altered by the intense supergene alteration can be identified.

The highly silicified and barren of ore minerals, Older Porphyry unit, is forming the craggy apex of Sac Hill as well as the rugged west-face at the exact center of the photograph. Between these two points and forming somewhat of a depression, is the altered and mineralized, Younger Porphyry unit, which hosted the Sacramento Pit, and to a lesser degree, the Lavender Pit.

The deeply eroded drainage to the left of Sac Hill is the trace of the massive Dividend Fault with nearly 1,000 meters of displacement. The footwall is pyritized and locally silicified Older Porphyry and Pinal schist.

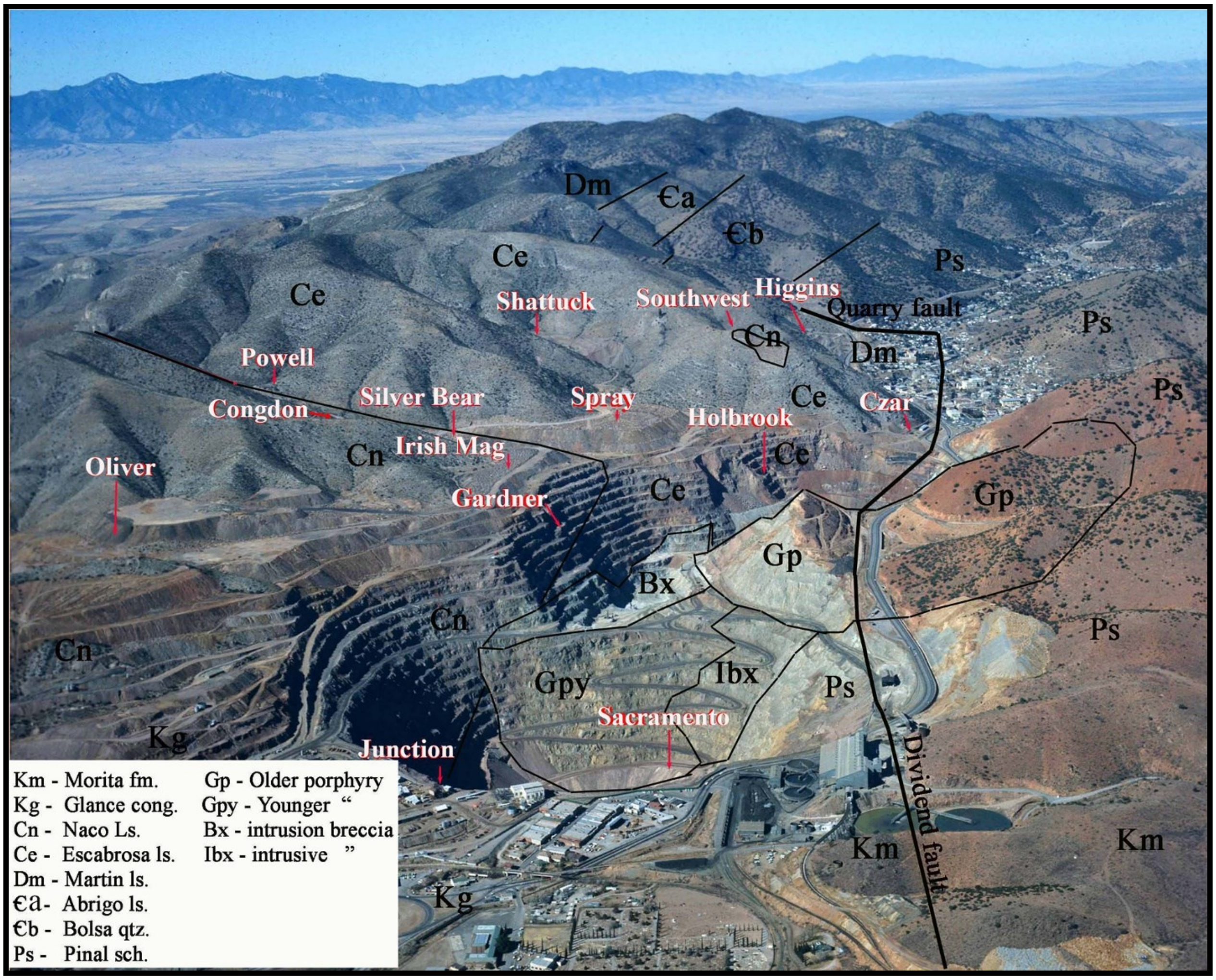
The topography low area in the foreground and continuing to the right, almost surrounding Sac Hill is an eroded area of the hydrothermally altered limestones, which intense and complete supergene alteration has converted to a mix of soft clays and iron oxides, hosting incredible orebodies. The buildings seen just to the lower, left of center are the infrastructure for the Holbrook mine, one of Bisbee's richest mines and a wonderful specimen producer. A few years after this photo was taken, the Holbrook shaft had to be replaced in hard limestone, as the ever-moving clays made the original shaft unsafe to use.

EARLY GEOLOGY STUDIES

Over the years, a number of competent individuals and groups studied the geology of Bisbee, beginning with Fredrick Ransome in 1904, whose excellent work served as the basis for subsequent efforts by Bonillas, Tenney, and Feuchere published in 1916, Carl Trischka's work in 1938, and that of Bryant and Metz, in 1966. Others have made important additional contributions over the years as well.

More recently, Cook (1994), Riggs (1994), Stegen et al. (2005), and a good summary by Schumer (2017) have added regional information as well as specific closeups, which have aided in the understanding of Bisbee's geology. Because of these fine treatments of this topic by those mentioned above, only a brief overview will be presented here to aid in understanding the mineralogy. It begins with the geologic history followed by descriptions of the various rock units and the structural geology. All of the above are noted again, along with others in Volume III.

GEOLOGIC HISTORY



Looking west at the Lavender pit with Bisbee in the background – 1974, general geologic features in approximate positions and mine sites indicated, P. Kresan photo.

Little can be reconstructed of the Precambrian other than to note that at some point after the regional metamorphism was completed, the resultant Pinal schist, which Meijer (2014) suggest: "*possesses many of the characteristics of rends a subduction complex associated with a Paleoproterozoic (1.64-1.7 Gy) Mazatzal volcanic arc"*. The Pinal was locally intruded by several basic dikes and eventually peneplaned. Much later, in mid-Cambrian times, marine deposition began during which nearly 400 meters of sediments were laid down, rapidly at first, then at a much slower rate.

There was a hiatus in the deposition from late Cambrian until upper Devonian times, or at least no evidence remains if any occurred. The rock record resumes with the Devonian seas deepening and the deposition of shaly to dolomitic limestone. During Mississippian times, the seas were much shallower, as evidenced by the numerous reef formations present in the Escabrosa limestone, which was deposited during this period. The deposition of limestone lasted through Pennsylvanian and into Permian times when uplift occurred.

The Paleozoic sediments had, by then, reached a total thickness of perhaps more than 2,000 meters and were undergoing extensive erosion. At some time during the late Triassic or early Jurassic times and while still relatively flat-lying, the sedimentary rock units underwent extensive faulting, and activity along the previously existing Dividend zone occurred once again, perhaps related to region-wide mid-Jurassic, arc-related volcanic events (Riggs et al., 1994).

The Sacramento Stock Complex development began about 200 million years ago when a quartz porphyry followed the course of the Dividend fault, intruding up through the schist and into the overlying sediments, even venting to the surface at some point, creating a topographic high (Hayes & Landis, 1964). This was the first of a multiphase igneous event as a part of the aforementioned mid-Jurassic, arc-related volcanic events (Riggs et al., 1994).

Next came a period of intense silicification of the existing parts of the Sacramento Stock Complex and, to a lesser degree and localized, the hosting sediments. Silica-rich solutions followed numerous structures for kilometers into the Paleozoic rocks resulting in local but intense silicification of the sediments. Silicification was quickly followed by heavy pyritization in the Older porphyry, schist and, silicified sediments. Immense masses of pyrite were deposited in the schist, and numerous, often massive replacement bodies of pyrite were scattered throughout the limestones. This forceful intrusion brecciated silicified Paleozoic sediments along several hundred meters of the contact, preparing it for high-grade mineralization.

Following the same path along the Dividend fault and close in time came another intrusive, the Younger porphyry, pushing its way alongside the first porphyry and spreading throughout the sediments for great distances as dikes. The related Warren and Cochise porphyries were emplaced at much the same time. Soon thereafter, intrusive breccia dikes and sills also invaded the sediments while an irregular pipelike mass of breccia more than 150 meters in diameter pushed its way into the stock. It is probable that this was contemporaneous with copper mineralization (Bryant, 1974). The silica breccias most probably formed at this time as well.

Four distinct pulses of mineralization occurred: (iron, sulfur, silica) - (iron, copper, sulfur) - (lead, zinc, iron, sulfur) - (copper, gold, silver, tin, bismuth, vanadium, tungsten, arsenic, antimony, tellurium, uranium), were deposited in varying amounts in the hundreds of isolated sulfide carbonate replacement deposits in the host limestones. Each pulse remobilized segments of the previous events to the point that, in some cases, significant portions were replaced or remobilized and deposited elsewhere. A wide variety of hypogene minerals, often in complex assemblages, were formed. Only the first two pulses of mineralization seem to have left their mark on the intrusive units of the Sacramento Stock Complex. However, the breccias in the complex were mineralized, to a very modest degree, by all events.

The sediments along the margins of the intrusives and breccia bodies were locally and irregularly metamorphosed and/or hydrothermally altered. Replacement by garnet, diopside, wollastonite and vesuvianite near the stock complex quickly gave way to tremolite, actinolite, and an edenite assemblage indicating only minor effects of high temperatures immediately adjacent to the stock complex. This assemblage, in turn, soon graded into recrystallized limestone and/or marble, followed by unaltered rock. In all, an irregular contact metamorphic halo of no more than 500 meters developed around the stock complex.

Metamorphic effects are also noted in the limestone along many, but not all, of the porphyry dikes. Generally, quartz is the most abundant alteration mineral, followed by epidote and garnet. No truly definitive pattern is evident in these instances because of the overlapping nature of the aureoles and the very irregular and erratic development of alteration minerals.

A large granitic mass, the Juniper Flat granite, was emplaced into the center of what would become the Mule Mountains. With this intrusion came numerous dikes penetrating the Precambrian rocks and the Paleozoic section for kilometers from this intrusive center. The K-Ar and Rb-Sr ages of biotite from the Juniper Flat granite are 163 Ma and 176 Ma, or Jurassic in age (Creasey and Kistler, 1962; Cook, 1994), respectively. Little to no alteration followed this intrusion; thus, the rocks remain much as emplaced. No influence from this stock or its dikes is found within the mineralized area. How this intrusion is related to the emplacement of the intrusions of the Sacramento Stock is uncertain, but it was probably comagmatic in origin (Bryant & Metz, 1966).

Before the Cretaceous period, regional uplift occurred, yet the sediments apparently remained reasonably flat. Aggressive erosion stripped an undetermined thickness of the Paleozoic sediments during this time, cutting deep canyons in the Sacramento Stock Complex, limestones, and mineralized areas.

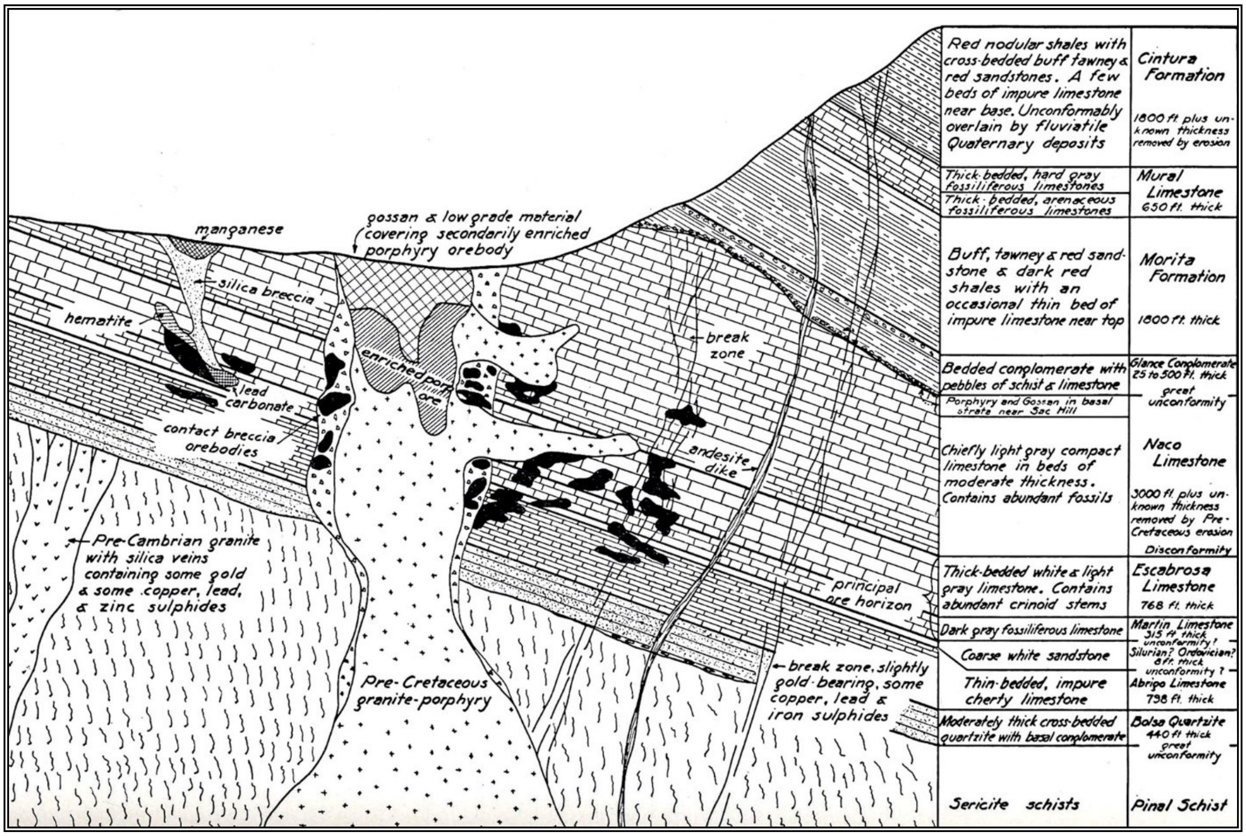
The first of several supergene events began soon after early-Cretaceous deposition because of the proximity to the surface, with oxidation occurring to variable depths in the limestone replacement deposits depending on the permeability of the controlling structures. A typical supergene chalcocite blanket was formed in the Younger Porphyry unit of the Sacramento Stock Complex that was more or less parallel to the pre-Cretaceous topography.

During early Cretaceous times, rejuvenation of the Dividend fault dropped the southern block 500 to 700 meters relative to the north side (Bryant & Metz, 1966). This seems to have interrupted supergene activity for a period.

To the south of the Dividend fault, the deep canyons were filled and the severe topography leveled by detritus material derived from the Sacramento Stock Complex as well as nearby mineralized limestone and material from the northern side of the Dividend as it was leveled by erosion, forming the Glance Conglomerate. Ultimately, the supergene alteration was stopped due to burial.

Subsequently, the area was covered by shallow seas, and the clastic Morita formation was deposited, followed by the rest of the sediments that make up the Bisbee group. However, a modest period of supergene alteration soon followed, with the most important effect being submarine diagenesis altering most of the early azurite to malachite.

With the close of the Mesozoic Era, the whole of southern Arizona was subjected to intense compression with thrust faulting of the Laramide orogeny. The Bisbee district acted as a single block (Bryant & Metz, 1966). Uplift allowed yet another period of supergene alteration to take place in the mid and western portions of the mineralized area.



Generalized geologic section, after Phelps Dodge (1938).

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 southwestern portion of the quadrangle and formed what we see today. The erosion again exposed the western part of the mineralized area to intense supergene activity, which was ongoing at the time of discovery, completing the formation of the mineral treasures the early miners found.

ROCK UNITS

PRECAMBRIAN ROCKS:

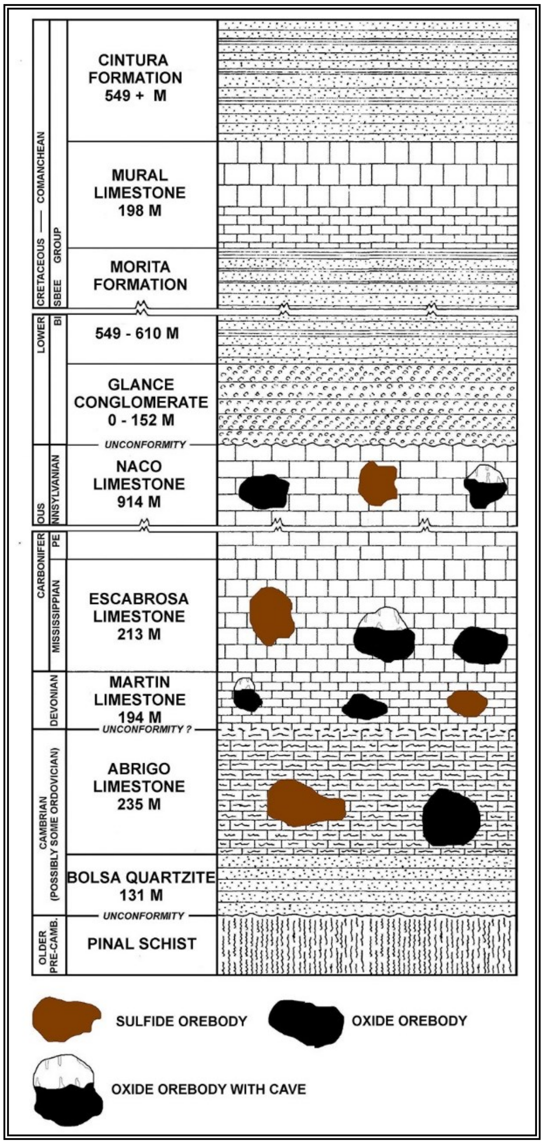
Pinal Schist:

This unit is the basement formation for much of southern Arizona and is of an unknown thickness at Bisbee. It has been dated at 1.7 Ga (billion years old). Essentially, the Pinal is a fine-grained, fissile, quartz-sericite schist that was most probably the result of regional metamorphism of thin-bedded, clastic sediments (Bryant & Metz, 1966). Thin and discontinuous quartzite beds occur within finer-grained schist units. Locally, the Pinal has been heavily mineralized with abundant pyrite and very minor copper sulfides. To this point, the Pinal schist has never been a host to economic mineralization, though the potential clearly exists, as this rock is host to about 15% of the chalcocite mineralization in the Cochise deposit (Stegen et al., 2005). This unit is most apparent in the hills north of Bisbee.

PALEOZOIC ROCKS:

Bolsa Quartzite:

Of middle Cambrian age (Bryant & Metz, 1966), this unit was deposited unconformably on the nearly level, peneplaned surface of the Pinal schist. The basal beds consist of a quartzite conglomerate that grades upward into a pebbly phase, then into a gritty, mostly argillaceous and calcareous phase, which grades into the overlying Abrigo limestone. Ransome (1904a) measured the Bolsa at 131 meters of thickness. While substantial pyrite occurs locally in the Bolsa, as do a very few small deposits of copper mineralization, it has never been an ore-producing horizon of note.



Generalized stratigraphic column. After Ransome, (1904) and Hogue and Wilson, (1950).
Redrawn by Douglas L. Graeme

Abrigo Limestone:

The Abrigo is of mid to late Cambrian age (Bryant & Metz, 1966) and achieved a total thickness of 235 meters (Ransome, 1904a). It sits conformably on the Bolsa and is a thin-bedded, impure limestone with three distinct units (Wiser, 1926). Occasional trilobites and brachiopods are the dominant fossils found in the Abrigo. A thin quartzite unit known in the district as the Parting Quartzite terminates the Abrigo at the top. The Abrigo was an important ore host for the underground mines at Bisbee, although its importance was not fully realized until the mid-1950s when the ores could be processed to remove the high-aluminum limestone that complicated direct smelting. Nye (1968) noted that 90% of the ore mined at that time was from the Abrigo. Substantial amounts of both primary sulfide and secondary oxide ores were mined from this unit.

Martin Limestone:

Upper Devonian in age and only 194 meters thick (Ransome, 1904a), this unit lies unconformably on the Abrigo. The Martin is a dark, somewhat shaly to thick-bedded limestone that is often dolomitic. It was the host to many sulfide replacement deposits and was the most economically important unit for the underground mines. This unit also hosted many oxidation caves, which were closely associated with the thoroughly oxidized ores in the western part of the district. It is quite fossiliferous locally, with the most common fossils as brachiopods, typically *Atrypa reticularis* and *Spirifer hungerfordi* (Ransome, 1904a).

Escabrosa Limestone:

This unit is of early to mid-Mississippian age and conformably overlies the Martin without a well-defined contact (Bryant & Metz, 1966). It is some 213 meters in average thickness and is generally light in color and thick-bedded. Impressive cliffs formed by the Escabrosa are evident on the south-facing slopes of the Mule Mountains near Bisbee. The unit is generally fossiliferous, with poorly preserved crinoid stems and corals locally abundant. The Escabrosa was also an important source of ore for the mining operations, producing substantial amounts of both sulfide and oxide ores. As an ore host, the most productive part of the Escabrosa was the lower 100 meters of the unit. Here, too, impressive oxidation caves developed over some of the wholly oxidized orebodies in the western part of the district.

Naco Limestone:

Ransome (1904a) named and measured this Pennsylvanian unit at 914 meters in thickness. Subsequently, Gilluly et al. (1954) divided this unit into six new formations, of which only the lower three are present at Bisbee (Bryant & Metz, 1966). These are the Horquilla, which conformably overlies the Escabrosa, the Earp, and, lastly, the Colina. No younger Paleozoic rocks have been recognized in the Warren Mining District (Bryant & Metz, 1966). Fossils are abundant as crinoids and brachiopods, and the formation can be distinguished from the crinoidal Escabrosa by the presence of fusulinids (Stegen et al., 2005). Only modest amounts of ore were ever discovered in these units. However, both sulfide and oxide ores were mined from the Naco, with oxidation caves associated with some of the oxide deposits.

MESOZOIC ROCKS

BISBEE GROUP:

Only a cursory overview of these post-mineral units is given, as they play but a very limited role in the important aspects of Bisbee's mineral fame. The lone exception might be the Glance Conglomerate that host the very fine Bisbee turquoise. Thus, it is treated separately under the turquoise discussion.

The Bisbee group of Cretaceous sediments sits on a very uneven erosional surface of Precambrian schist, Paleozoic sediments, and intrusives. The oldest unit in this post-ore group is the basal Glance conglomerate. In the Lavender pit area, the Glance is purple/brown color with clasts of Pinal schist, all of the Paleozoic units and, the whole suite of Sacramento Stock Complex units of deeply oxidized igneous rocks, breccias and ore fragments.

The limestone clasts in the lower Glance are often mineralized and oxidized with gossan features, copper oxide, and carbonates, as well as iron and manganese oxides, and mixed with limestone clasts that are not altered. The matrix of the conglomerate is composed of rock flour derived from the lithologies observed in the clasts.

The Glance is overlain by the Morita sandstone, then the cliff-forming Mural Limestone, which dominates the horizon above Lowell. Lastly, the Cintura sandstone/shale is on top for a total thickness of at least 1,500 meters.

Other than a few small and scattered slightly mineralized quartz outcrops in the eastern part of the district, no mineralization is known to occur in these Cretaceous rocks. These post-Cretaceous silicas or "boxwork" silica outcrops on largely vertical structures may contain very modest pyrite and sparse galena, sphalerite, chalcocite or, chalcopyrite (Trischka, 1938), with modest amounts of gold. These silica outcrops may be an indication of fluid flow through the rocks after Laramide(?) tilting of the Cretaceous rocks (Stegen et al., 2005).

IGNEOUS ROCKS:

Juniper Flat Granite:

This granitic rock is most prominent to the north and west of the town of Bisbee, where it is the dominant physiographic feature and forms impressive tan to pink cliffs. The rock, which has coarse-grained to porphyritic textures, is pink to purplish-gray in color. Usually fresh and free of alteration, the Juniper Flat granite is dated at 176 million years (Creasey and Kistler, 1962). Numerous related and associated dikes and sills have intruded all of the pre-Cretaceous rocks as well. Very small, localized gold and gold/copper deposits have been mined from this granite over the years.

Sacramento Stock Complex:

The term complex is used to describe the Sacramento Stock as it is actually composed of several distinct porphyry units as well as a variety of breccias. The older of the four intrusives is a highly altered quartz porphyry, which was intensely silicified and pyritized with 15 to 18 percent pyrite by the first phase of mineralization (Bryant & Metz, 1966) and was almost totally devoid of hypogene ore minerals. Apparently was sealed during early alteration, precluding mineralization by later ore-bearing fluids. Much of what remains of Sacramento Hill is composed of this unit. Lang (2001) dates the older porphyry at 198.9 Ma. Others have reported a younger date, as is noted below.

The intrusion of this first porphyry also caused the development of a large intrusion breccia in the country rock along the south side of the stock, which became very well mineralized by all of the four subsequent mineralizing events. It was an extremely important source of ore for the underground mining as well as the two open-pit mines. This breccia is described in further detail below.

The Younger Porphyry intrusive is described as a quartz-feldspar porphyry (Bryant & Metz, 1966). It was moderately altered, first by hydrothermal fluids and then by several periods of supergene activity. This unit was reasonably well mineralized by two of the events and was the principal source of ore for both open pit mines. This may well be the same unit that is found in the underground mines as numerous dikes, though there are modest differences. A very large intrusive breccia followed this last intrusive event, which is described in the next section.

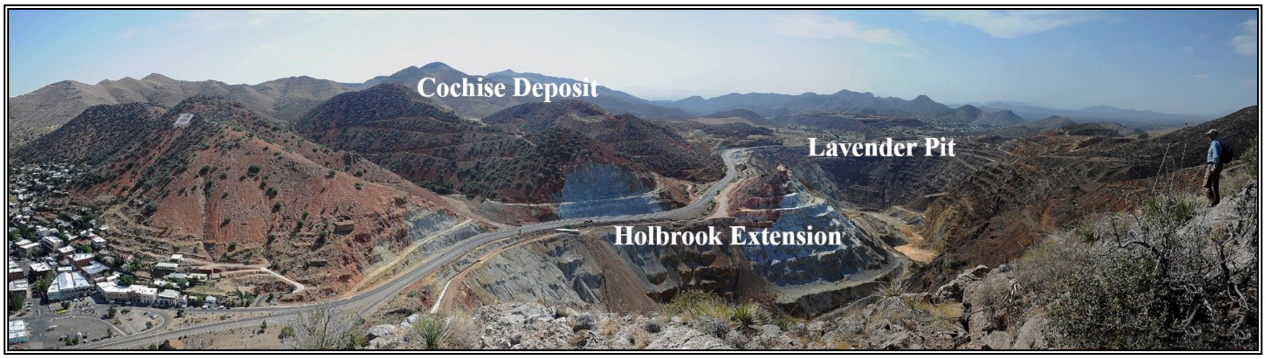
Both of the aforementioned intrusive units have been dated at 180 ± 3 million years (Phelps Dodge, personal communication, 1972). Lang (2001) dates them at 198 m.y.a and 199 MYA. Lowell and Guilbert (1970) ascribed the even younger age of 163 million years to these units.

Recent data gathered from drilling and mapping programs have demonstrated the existence of at least two additional intrusive phases (Stegen et al., 2005). There is a stock-like mass beneath the Lavender pit, which has been named the "Warren porphyry." The Warren porphyry was intersected by a drill hole beneath the bottom of the Lavender pit from 15 XC on the 3100 level of the Campbell Mine. One of the authors (RWG III) was involved in this drilling program and recognized it as a distinctive intrusion, though its lithology was determined much later.

The Warren porphyry is a biotite quartz monzonite porphyry with 50% plagioclase and 7.5% biotite phenocrysts in a groundmass of quartz and orthoclase. The rock contains disseminated chalcopyrite with lesser pyrite and minor molybdenite, something unusual for Bisbee (Stegen et al., 2005). The presence of molybdenite distinguishes it from the other porphyries, as, unlike most other copper porphyries, molybdenite is rare in the Bisbee porphyries. A single sample from this unit has a U-Pb date of 201.4 + 0.8 Ma (Lang, 2001), who believes it to be a part of the Younger porphyry.

What has been named the "Cochise porphyry" is in the Cochise deposit area. It is exposed as dikes in the northern side of the district, from Chihuahua Hill to Copper King Hill, where it consists of coarse-grained biotite granodiorite with weakly disseminated pyrite and chalcopyrite

(Stegen et al., 2005). Recent mapping and drilling suggest that this dike connects at depth with a stock drilled in the Cochise area by Occidental Minerals in 1974. Lang (2001) reported a U-Pb date of 200 + 0.8 Ma for the Cochise porphyry.



Panorama view looking more-or-less east from Queen Hill, and showing the location of the Cochise deposit relative to the Lavender Pit and Holbrook Extension. Graeme/Larkin collection

Lowell Volcanics:

The erosional remnants of a probably Jurassic-aged volcanic tuff-cone unit have recently been recognized. This poorly described unit occupies a very limited area below the Glance Conglomerate in and adjacent to the Lavender Pit Mine, extending as far east as to at least the Junction shaft, which cut about 30 meters during shaft sinking.

A wedge-shaped outcrop exposed in the hanging wall of the Dividend fault on the south side of Highway 80, as well as a small outcrop along the private road to the Denn mine, are the known exposures. This unit consists of a basal breccia overlain by a coarse pumice tuff, which, in turn, is then overlain by a crystal-lithic tuff containing feldspar phenocrysts and small lithic fragments. The tuff is cut by an intrusive breccia, feldspar quartz porphyry, and is modestly mineralized by chalcopyrite, bornite, and pyrite. The tuff is also strongly altered to a quartz/sericite assemblage (Stegen et al., 2005).

The rock has not been dated, but its relationship to other geologic units is clear, as it rests atop eroded Paleozoic limestone and is overlain by the Cretaceous Glance Conglomerate. Presumably, it is subaerial ejecta from some phase of the Sacramento Stock Complex development, reflecting the venting of at least one phase of intrusion.

BRECCIAS:

Breccias are included here because of their abundance, obvious importance to ore deposition, and their direct association with intrusive action. In-depth information on the breccias at Bisbee, the evolution of understanding as to their geneses, and their role in mineralization can be found in Bonillas et al. (1916); Trischka (1928), (1938); Bryant & Metz, (1966), and Bryant, (1964), (1968), (1974). At Bisbee, the more important breccia types were referred to as intrusion, intrusive, and silica breccias.

Intrusion Breccias:

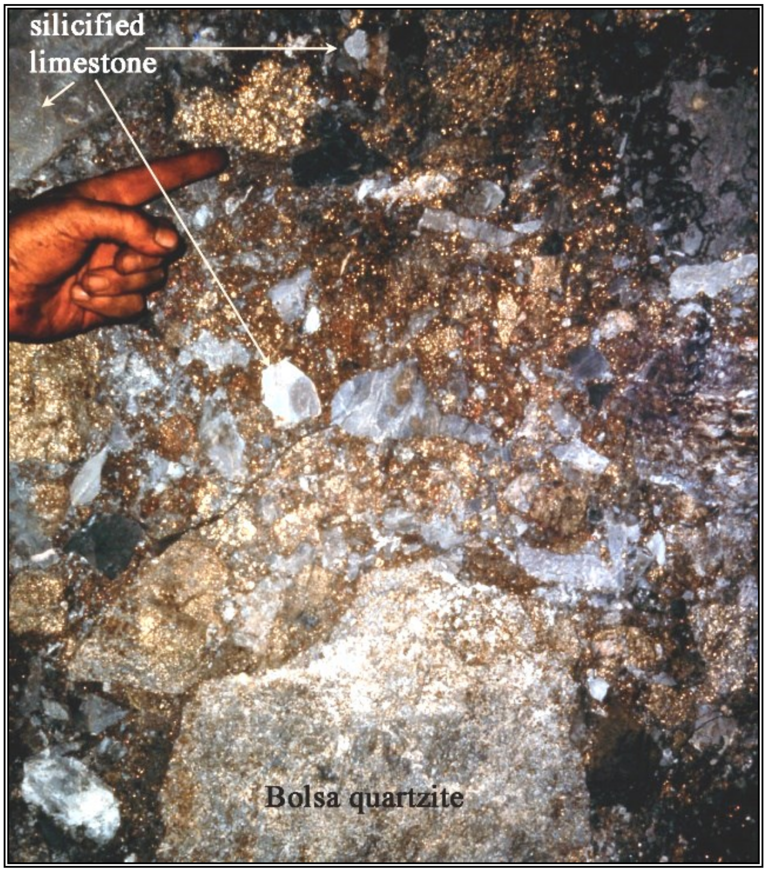
Early workers at Bisbee referred to this as the "contact" breccia, as it occurred at the contact of the Paleozoic limestones with the Sacramento Stock Complex, particularly the Younger porphyry. It covered a large area and very much appeared to have formed by the forcible intrusion of the Older porphyry, which seems to have been dragged or pushed in from depth (Bryant & Metz, 1966). It is composed of often-large silicified angular to rounded fragments representing every pre-Cretaceous unit except the porphyries and typically grades into undisturbed wall rock. The matrix of this unit consists of siliceous rock flour and locally, sulfides, with brecciated fragments of the various rock units, many of which were replaced by sulfide minerals as well. This breccia was extremely important as a source of ore, both in the underground mines and the two open pits.

Intrusive Breccias:

Also called the Lavender Pit intrusive breccia because of its prominence in the pit. However, this breccia type was found throughout the district in both the underground mines and as an important component of the Sacramento Stock complex. The size of the intrusive breccia masses was highly variable and could be as little as 5 mm thick to as much as 150 meters.

They were a heterogeneous mixture of all pre-Cretaceous units, including the Older porphyry in a matrix of rock flour, which locally contained appreciable sulfides. The fragments were angular to rounded and have been found up to more than 30 meters in size.
Bryant (1968) initially ascribed a fluid intrusion origin to these breccias and estimated that more than 80 million cubic meters of such breccias had been emplaced.

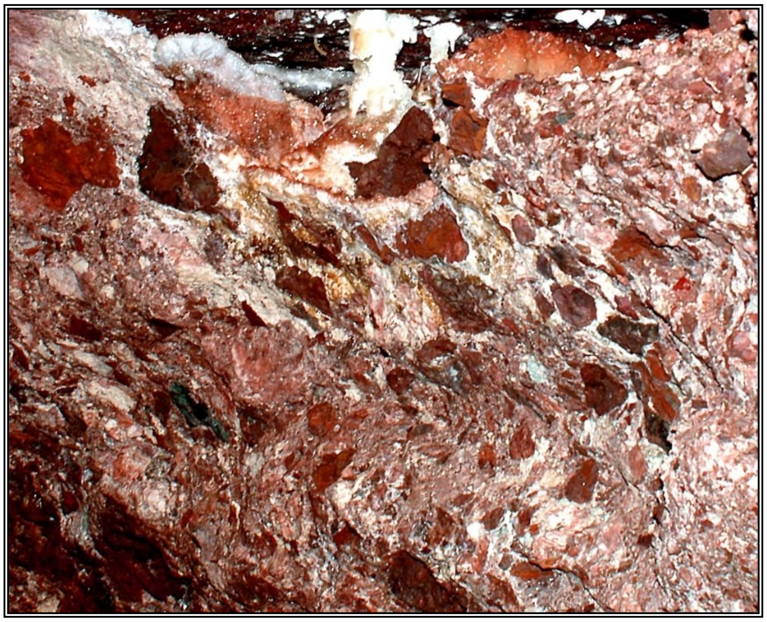
Later, Bryant (1974) suggested that the sulfides were contemporaneous with the emplacement of these breccias and that they may well be considered "ore magmas," in which the transporting media was a circulating hot water slurry in a fine-grained or rock-flour matrix of pulverized rock and sulfides.



Pyrite replaced fragments, silicified limestone fragments and a large Bolsa quartzite fragment, in intrusive breccia on the 1600 level, Campbell Mine. Graeme/Larkin collection.

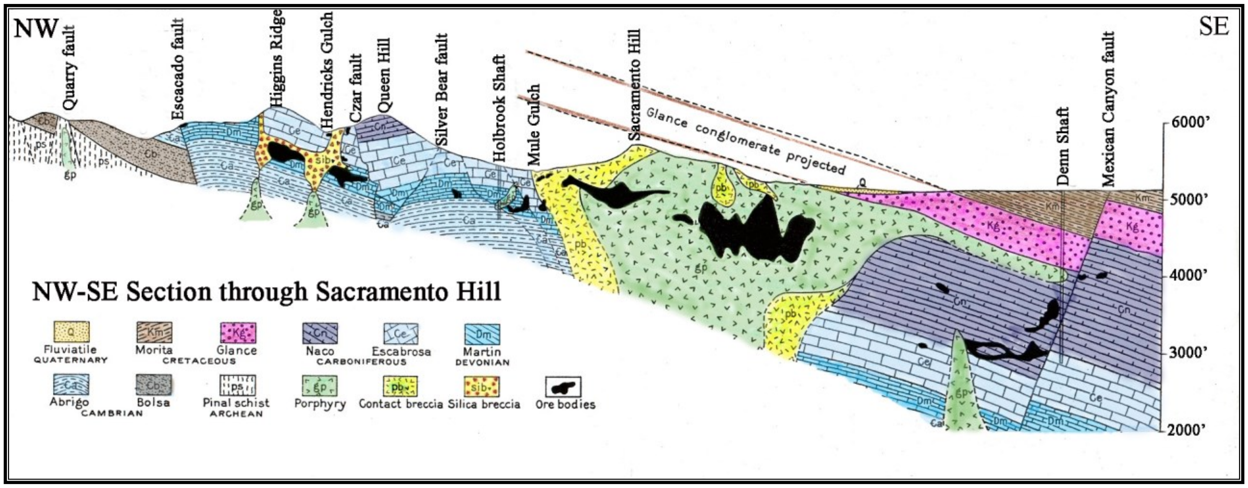
Silica Breccias:

As the name suggests, these were very siliceous units. They were composed of highly angular fragments of limestone, which had been completely replaced by silica in a matrix of cryptocrystalline quartz and specular hematite. Open spaces were often calcite-lined. Relict fossils were not uncommon and represented all of the fossiliferous units in the area of the breccia. These fossils indicate that movement has occurred both up and down as well as laterally. These units were apparently restricted to the Paleozoic limestones in the Southwest, Shattuck, and Higgins's ore zones and were invariably pipelike, and connections with porphyry at depth were believed to occur (Bonillas et al. 1916). Trischka (1932) estimated that 90 percent of the ore mined in these areas was in physical contact with silica breccias. The origin of these breccias remains unclear, as does the time of emplacement.



Left: Silica breccia with a calcite decorated void, 7th level, Southwest Mine, view- 4.3 meters. Apparent flow features and clast alignment are obvious. Graeme/Larkin collection.

STRUCTURAL GEOLOGY



Geologic cross section looking north east, showing the possible silica breccia connection with intrusives, after Bonillas, et al. (1916).

Nye (1968), in his excellent, detailed study of the structure at Bisbee, summarized the development of the dominant structure as *"... upward pressure from a batholith underlying the Mule Mountains domed the schist and Paleozoic rocks, with consequent rupture along the crest of the Bisbee anticline and formation of the Dividend fault zone. The development of the rest of the fault system followed with steplike down dropping of fault blocks to the southwest and southeast from a point near the southern end of the Juniper Flat stock ..., being interrupted in places by slumping of blocks along antithetic faults. The northeast-trending transverse faults were generally active later than the parallel and diagonal faults, as they cut the latter structures in most cases. Structurally, the northwest-striking, south-dipping Dividend fault zone is the most obvious and important feature in the district. It is an ancient structure, one that has apparently experienced numerous periods of activity, both before and following the intrusion of the Sacramento Stock Complex, for which it was the conduit, and the mineralization of the sediments."*

In a bit more detail, the Dividend Fault divides the Mule Mountains along their major axis from the mouth of Mule Gulch to the beginning of Tombstone Canyon, where it becomes indistinguishable near the Quarry fault. It is a normal fault, trending northeast with a southeasterly dip of from 60° to near vertical. At its easternmost exposure, nearly 1,500 meters of displacement can be measured, while more than 600 meters of movement has occurred at the west, where it meets the Quarry fault. Displacement is unmeasurable westward past the Quarry fault, as both hanging and footwall are in Pinal schist.

Underground, this fault zone ranges from just over 10 meters wide to nearly 80 meters. From the edge of the Sacramento Stock Complex, almost to the Czar shaft, it contained substantial high-grade material in the gouge, as supergene copper carbonates, oxides and, sulfides. However, as it was so broken, altered, and often near-fluid in nature, mining the Dividend zone was difficult and treacherous. Indeed, it was never completely mined underground. Open pit mining did remove a good bit that was left by the failed underground efforts. However, it was so full of mine timber that it caused trouble at the smelter. This was "direct smelt" ore (sent directly to the smelter, not concentrated).

The Quarry fault is the western limit for mineralization as well as the western-most fault in a series of north-northeast trending fault zones that are more or less perpendicular to the Dividend fault zone. From west to east, the more important of these structures are the Quarry, Escacado, Czar, Shattuck, Silver Bear, Mexican Canyon, and Campbell. Ore occurrence was intimately associated with these structures (Bryant & Metz, 1966), as is so evident in the previous cross-section.

Generally, these faults dip steeply to the west with a variable displacement of tens of meters to more than 150 meters, as in the case of the Mexican Canyon fault. They have strike lengths measured in hundreds of meters. Nye (1968) concluded that the faults formed prior to ore deposition, using pyrite occurring as fragments in fault breccia and as a replacement of the gouge, with chalcopyrite typically replacing the pyrite as evidence. Some four kilometers to the south and sub-parallel to the Dividend zone is the Escabrosa fault zone. It is here that most of the north-northeast faults terminate, and no ore has been identified south of this feature. A few sinuous structures with a generally northwest trend and largely parallel to the

Dividend/Escabrosa faults lie between these structures. This formed the "Copper Queen graben" of Nye (1968).

The breaking, fracturing, offsetting, and the opening of bedding plans by the tectonic actions which generated the structures noted above and the many others unnamed were effectively the ground preparation, which allowed for mineralization. Nye (1968) suggests; *"Hydrothermal fluids escaping from magmas below entering the broken zones underwent a sudden loss in pressure, with a lowering of temperature due in part to adiabatic expansion and in part to the cooling effects of the rock… may have contributed to the displacement of equilibrium within the hydrothermal fluids, allowing reaction with, alteration, and replacement of the wallrock by sulfides*."

MINERALS

This short section, which touches on the minerals recognized as occurring at Bisbee, is intended to place the minerals in the context of the geology of their formation. Volume II of this series discusses each species in detail, including information about the occurrences for each species.

ROCK-FORMING MINERALS:

The rock-forming minerals at Bisbee are, in general, typical of this part of Arizona. They are less than spectacular both in their form and in occurrence. Quartz is a primary constituent of the several quartzite units in the Paleozoic and Cretaceous sediments, as well as the basement, Pinal schist. Thus, quartz is both abundant and widely distributed. Calcite and dolomite are the dominant rock-forming minerals present as the principal constituents of the Paleozoic, Mesozoic, and Cretaceous limestone units. Epidote is a common constituent of certain parts of the Abrigo, which Bonillas et al. (1916) suggested formed as an alteration of impure beds caused by burial and not by the intrusions or hydrothermal alteration. The Precambrian Pinal schist, which underlies the Paleozoic limestones, contains abundant muscovite and quartz as alteration products of unknown minerals developed during the original metamorphism.

albite
allanite
augite
"biotite"
calcite
celadonite
chromite
dolomite
enstatite
epidote
fluorapatite
fluorite
glauconite
hydrobiotite
ilmenite
magnetite
marcasite
microcline
muscovite
"oligoclase"
orthoclase
plagioclase
quartz
rutile
sanidine
schorl
zircon

Table 1: The rock-forming minerals recognized at Bisbee.

In the two intrusive units, as well as several breccias of the Sacramento Stock Complex, quartz is abundant. Also, several of the feldspars were common; however, most were altered to any number of clay or clay-like species, leaving little of the original mineralogy of the rock evident, except for the quartz and a few minor accessory minerals.

Host rock-forming minerals, which make up the Juniper Flat granite, are microcline, orthoclase, plagioclase, biotite, and quartz. These minerals are generally fresh and relatively free of alteration, unlike those in the Sacramento Stock Complex. A number of accessory minerals are also associated with the dominant species.

HYDROTHERMAL ALTERATION MINERALS:

The hydrothermal alteration associated with the intrusions and the several phases of mineralization was limited, considering such an expansive series of deposits and the number of mineralizing events. Hydrothermal alteration of the limestones surrounding the Sacramento Stock Complex was typically localized and modest. It was characterized by Bonillas et al. (1916) as one of abundance and persistence rather than great intensity. No high-temperature minerals were developed in any significant amount, or if they did, they were subsequently replaced. Minerals like garnets, diopside, wollastonite, scapolite, and vesuvianite have been noted (Bonillas et al. 1916), but only in minimal amounts.

The intrusion breccia zone around the stock complex is generally marked by extreme amounts of silica, which has replaced all other gangue and rock-forming minerals for a short distance. Pyrite, then sericite, are the next most abundant, with chlorite also reasonably common in the intrusion breccias. There are large areas of intergrown magnetite, hematite, and pyrite associated with this breccia, reflecting retrograde alteration. This is where the best-formed garnets and wollastonite are found. Substantial amounts of copper, lead, and zinc sulfides were also locally abundant in this zone. Some extremely rich ores were mined from scattered areas in this breccia.

In the transition from the contact zone into the limestone country rocks that hosted the many replacement deposits, the un-brecciated contact limestones altered differently as a function of their composition. The Abrigo and lower Martin altered to masses of sericite, chlorite, calcite, and quartz, while the Escabrosa and Naco usually had just a narrow fringe of metamorphic minerals with the mass simply recrystallized (Bonillas et al., 1916).

Outside of the contact areas, the limestone was occasionally altered with no apparent relation to any intrusive or mineralization. Recrystallization, and to a lesser degree, marbleized rinds around sulfides were the most common such alteration. However, in many, if not most cases, the copper ores were present with a little apparent associated alteration. In fact, so little alteration of these limestones took place that it was usually impossible to use it as a prospecting guide. One could be just a few centimeters from an orebody and not be able to see any difference in the nature of the country-rock.

Alteration of the several units in the Sacramento Stock was variable and often intense. Bryant and Metz (1966) report that what they call the Older Porphyry unit was so altered that the original rock type cannot be determined.

The Younger Porphyry was less altered, and this alteration was primarily restricted to the formation of clays and claylike minerals from the feldspars. Little, if any, in the way of collector specimens of interest was formed by these processes at Bisbee. The many intrusive dikes found in the underground mine workings are invariably highly altered, so much so that the original lithology and mineralogy have often been totally obscured.

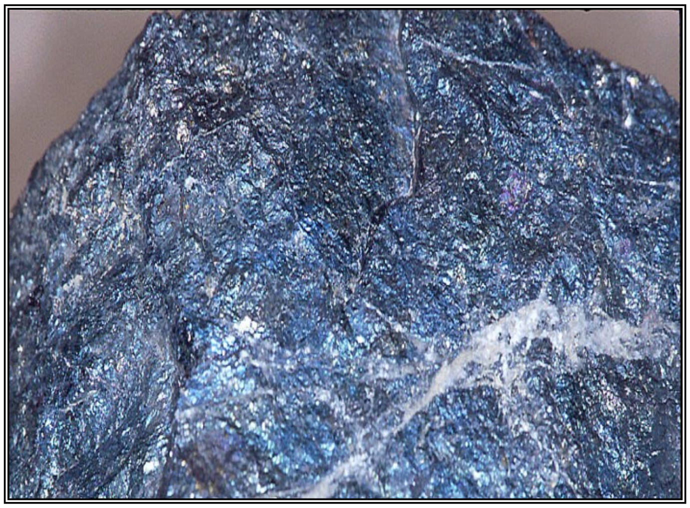
actinolite
allophane
alunite
anatase
andradite
antigorite
"biotite"
bixbyite
brookite
brucite
calcite
celadonite
chamosite
chrysotile
clinochlore
clinochrysotile
clinozoisite
diaspore
dickite
diopside
dolomite
edenite
endellite
epidote
forsterite
gormanite
grossular
halloysite
hematite
hydrobiotite
illite
ilmenite
kaolinite
laumontite
lepidolite
magnesite
magnetite
meionite
melonite
muscovite
natrolite
pectolite
prehnite
pumpellyite
pyrite
pyrope
pyrophyllite
quartz
rutile
sepiolite
spessertine
stevensite
talc
thomsonite
titanite
tremolite
vesuvianite
wollastonite
zircon
zoisite

Table 2: The hydrothermal alteration minerals recognized at Bisbee.

HYPOGENE ORE MINERALS:

Two important but distinct ore mineral domains are found at Bisbee from a hypogene, economic mineralization standpoint. These are, first, the mineralized parts of the intrusive complex of the Sacramento Stock, along with the intrusion breccias albeit, supergene enrichment enhanced the copper grade to make a great deal of these intrusive units economic. Secondly, and economically far more important, there are the many isolated sulfide carbonate replacement deposits.

The basic economic mineralogy of the two domains is distinctly different, in the most general of terms. Detailed information on both of these depositional environments can be found in Bonillas et al. (1916) and Bryant and Metz (1966), as well as discussed later in this work.
Multiple, high-sulfur but otherwise chemically diverse pulses of mineralization occurred, reacting both with the host rock and the earlier emplaced minerals. In the replacement deposits, each successive pulse left its imprint on the minerals of the previous events, ultimately forming a broad suite of complex minerals, largely masked by the common ore minerals.

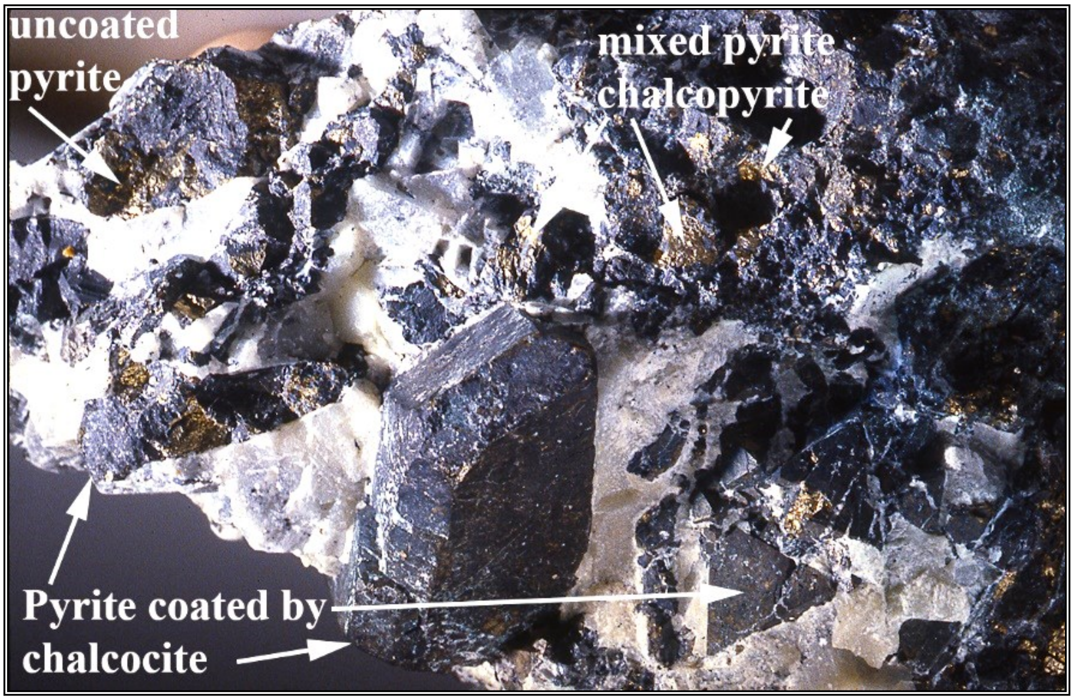


Right: Typical massive bornite with quartz and very minor pyrite, 2700 level, Campbell Mine–view– 8 cm. Graeme collection.

Indeed, for many years, the hypogene mineralogy was viewed as straightforward and relatively simple. The works of Bonillas et al. (1916), Hogue and Wilson (1950), Bryant and Metz (1966) as well as Graeme (1981) reflected this understanding. The occasional presence of anomalous elements was poorly understood. The development of advanced detection equipment opened the door to a new world of complex mineral species hidden as inclusions in the abundant, common sulfide ores and gangue minerals. A wide variety of species containing antimony, arsenic, bismuth, tellurium, tin, tungsten, uranium, gold, silver, and vanadium were found.

acanthite
aikinite
alabandite
altaite
anhydrite
arsenic
arsenosulvanite
barite
bismuth
bismuthinite
bismutite
bogdanovite
böhmite
bornite
calaverite
calcite
canfieldite
cassiterite
chalcocite
chalcopyrite
chrysotile
cinnabar
colusite
cosalite
covellite
cupropavonite
digenite
djurleite
dyscrasite
emplectite
enargite
famatinite
fluorite
forsterite
freibergite
galena
gold
goldfieldite
greenockite
hausmannite
hematite
henryite
hessite
hocartite
hodrushite
hübnerite
jacobsite
jalpaite
kësterite
kettnerite
kiddcreekite
kostovite
krennerite
ktenasite
kuramite
luzonite
magnetite
marcasite
matildite
mawsonite
molybdenite
nekrasovite
neltnerite
nolanite
pearceite
petzite
polybasite
pyrargyrite
pyrite
pyrrhotite
quartz
rhodonite
rhodochrosite
rhodostannite
rickardite
roscoelite
rucklidgeite
scheelite
siderite
silver
sphalerite
spionkopite
stannite
stannoidite
stibnite
stromeyerite
stützite
sylvanite
tellurium
tellurobismuthite
tennantite
tetradymite
tetrahedrite
uraninite
velikite
volkonskoite
volynskite
wittichenite
“wolframite”
yarrowite

Table 3: The hydrothermal ore and gangue minerals recognized at Bisbee.



Younger Porphyry ore sample consisting of quartz, unidentified clays, minor chalcopyrite and pyrite coated with supergene chalcocite. It is only because of the supergene chalcocite that this was of ore grade (>0.35 % Cu). View-8 cm. Lavender Pit Mine, Graeme collection.

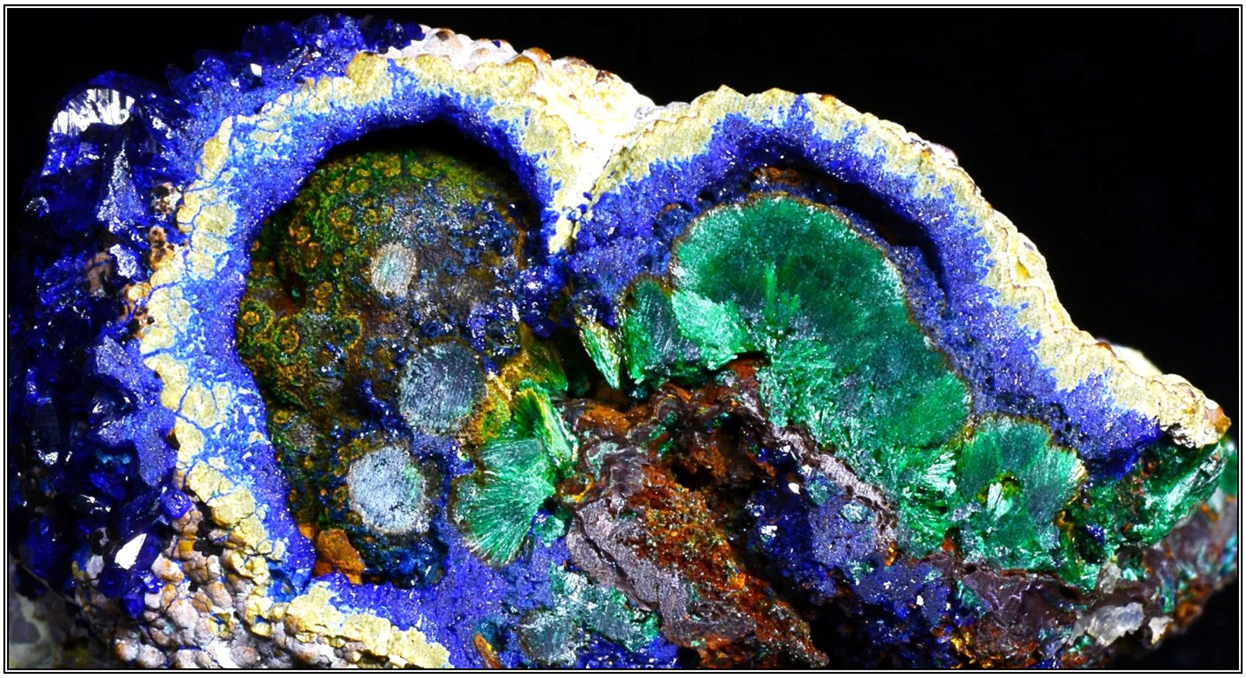
The mineralogy of the Sacramento Stock Complex is generally similar to any small-sized copper porphyry, as so frequently seen in the Basin and Range geologic provenance. The near-total lack of molybdenum is a significant difference from other regional copper porphyry deposits.

High pyrite, silicification, and modest amounts of copper/iron/sulfur minerals were present in the Younger Porphyry, which was made economical by supergene activity. Almost no lead/zinc minerals were deposited, except locally in the breccias. Species related to the modest, late-stage, multi-element episode of mineralization have not been recognized in any of the intrusive units.

SUPERGENE MINERALS:

There is little doubt that some of the supergene species from the Warren Mining District at Bisbee are among the finest of their kind in the world. The unparalleled variety in form and color in which several of the more important species occur has added to the fame of Bisbee as a producer of magnificent minerals.

The variety of minerals formed under supergene conditions at Bisbee reflects a wide range of, often-isolated, depositional environments. In most instances, these environments changed over time as oxidation progressed deeper. However, in a number of instances, because of burial by post-ore sediments, tilting, and/or uplift, earlier formed supergene minerals were subjected to moderate to low pH (acidic) solutions of variable chemistry, which followed new solution paths created by tilting. This interaction often formed a different suite of species at the expense of the earlier supergene minerals.



An example of multiple depositional events of varying chemistry beginning with hard, low pH goethite, grading into soft, moderate pH goethite. These are followed by subaqueous deposited malachite, which shows etching by iron-rich, lower pH solutions. Soft goethite was washed from the empty spaces. Azurite of subaqueous origin was next. Later, gibbsite coated the azurite in an open-air environment and dried, leaving shrinkage cracks. Subaqueous azurite filled the cracks and locally deposited 4 mm crystals. View – 2.7 cm, Holbrook Mine, Graeme collection.

Below is a list of those species recognized as having formed under supergene conditions. Some of the below-listed species have other, perhaps more common, modes of occurrence but are included here for completeness.

allophane
alunite
anglesite
antlerite
aragonite
atacamite
aurichalcite
austinite
azurite
barite
basaluminite
bayldonite
bayleyite
beaverite
beudantite
bindheimite
bisbeeite
bismite
bismutite
böhmite
bornite
botallackite
braunite
braunite II
brochantite
bromargyrite
buttgenbachite
calcite
caledonite
carbonate-cyanotrichite
cerussite
cesárolite
chalcanthite
chalcoalumite
chalcocite
chalcophanite
chalcophyllite
chalcopyrite
chalcosiderite
chlorargyrite
chrysocolla
claringbullite
clinoatacamite
clinoclase
conichalcite
connellite
copper
coronadite
covellite
crednerite
cryptomelane
cuprite
cuprotungstite
cyanotrichite
delafossite
descloizite
devilline
digenite
dioptase
djurleite
dolomite
duftite
eddavidite
endellite
eugenite
ferrimolybdite
fornacite
galena
gerhardite
gibbsite
goethite
gold
graemite
graphite
groutite
gypsum
halloysite
hematite
hemimorphite
hetaerolite
hisingerite
hoganite¿?
hydrocerussite
hydrohetaerolite
hydrozincite
iodargyrite
johannite
jarosite
kaolinite
kettnerite
ktenasite
langite
leadhillite
lepidocrocite
linarite
liroconite
malachite
manganite
massicot
miersite
mimetite
minium
mottramite
murdochite
nambite
nantokite
neltnerite
opal
osarizawaite
paramelaconite
paratacamite
paratellurite
pharmacosiderite
phosgenite
planchéite
plattnerite
plumbojarosite
powellite
pseudomalachite
pyrite
pyrolusite
pyromorphite
quartz
ramsdellite
ralstonite
romanèchite
rosasite
scorzalite
sengierite
sepiolite
shattuckite
siderite
silver
smithsonite
spangolite
spertiniite
sphalerite
spionkopite
stibiconite
stolzite
stromeyerite
sulfur
tangeite
teineite
tellurite
tenorite
tilasite
tolbachite
torbernite
turquoise
tyrolite
tyuyamunite
uranopilite
vanadinite
variscite
volborthite
willemite
wulfenite
zippeite

Table 5: Supergene mineral species recognized at Bisbee

POST-MINING MINERALS:

A large number of minerals have formed in the mines of the district, following the opening of the ground through mining, thus, the term post-mining. For the most part, the development of post-mining minerals was the direct result of the introduction by the mining of a near-surface, oxygen-rich environment to the sulfides. Both hypogene and supergene sulfides were altered by the introduction of these conditions, often quickly.

Many of the post-mining minerals found here have been recognized only in this type of depositional environment, while others are known to form under typical supergene conditions as well. It is, however, reasonable to assume that the majority of these species also occurred as a part of normal supergene processes, but were not noted. This lack of recognition was probably a function of their nondescript appearance and typically high solubility. A list of those species recognized as forming under post-mining conditions is presented below.

alunogen
anglesite
anhydrite
anthonyite
antlerite
aragonite
aurichalcite
azurite
bianchite
bilinite
boothite
botryogen
brochantite
calcite
chalcanthite
chalcocite
chrysocolla
copiapite
copper
coquimbite
cuprite
cuprocopiapite
epsomite
felsőbányaite
ferricopiapite
fibroferrite
goethite
goslarite
gypsum
halloysite
halotrichite
hexahydrite
hydrobasaluminite
ilsemannite
jokokuite
malachite
melanterite
metavoltine
paratacamite
paracoquimbite
pickeringite
ransomite
plumbojarosite
rhomboclase
römerite
rozenite
siderotil
sulfur
szomolnokite
voltaite
zincobotryogen
zincocopiapite

Table 6: Post-mining mineral species recognized at Bisbee

Post-mining boothite on decomposing pyrite, in situ. View-13 cm, 7th level Southwest Mine, Graeme/Larkin collection.

acanthite
actinolite
aikinite
alabandite
albite
allanite-(Ce)
allophane
altaite
alunite
alunogen
anatase
andradite
anglesite
anhydrite
ankerite
anthonyite
antigorite
antlerite
aragonite
arsenic
atacamite
augite
aurichalcite
austinite
azurite
bandylite
barlowite
baryte
bayldonite
bayleyite
beaverite-Cu
beudantite
bianchite
bĺlinite
bindheimite?
“biotite”
“bisbeeite”
bismite
bismuth
bismuthinite
bismutite
bixbyite
bogdanovite
böhmite
boothite
bornite
botallackite
botryogen
braunite
“braunite II”
brochantite
bromargyrite
brookite
brucite
buttgenbachite
calaverite
calcite
caledonite
canfieldite
carbonatecyanotrichite
cassiterite
celadonite
cerussite
cesárolite
chalcanthite
chalcoalumite

chalcophyllite
chalcopyrite
chalcosiderite
chalcostibite
chamosite
chlorargyrite
chromite
chrysocolla
chrysotile
cinnabar
claringbullite
clinoatacamite
clinochlore
“clinochrysotile”
clinoclase
clinozoisite
colusite
conichalcite
connellite
copiapite
copper
coquimbite
coronadite
cosalite
covellite
crednerite
cryptomelane
cuprite
cuprocopiapite
cupropavonite
cuprotungstite
cyanotrichite
delafossite
descloizite
devilline
diaboleite
diaspore
dickite
digenite
diopside
dioptase
djurleite
dolomite
duftite
dyscrasite
edenite
emplectite
enargite
eddavidite
“endellite”
enstatite
epidote
epsomite
eugenite
famatinite
felsőbányaite
ferricopiapite
ferrimolybdite
fibroferrite
fluorapatite
fluorite
fornacite
forsterite
freibergite
furutobeite
galena

glauconite
goethite
gold
goldfieldite
gormanite
goslarite
graemite
graphite
greenockite
grossular
groutite
gypsum
halloysite-10Ǻ
halotrichite
hausmannite
hematite
hemimorphite
henryite
hessite
hetaerolite
hexahydrite
hisingerite
hocartite
hodrušhite
hoganite**¿?**
hübnerite
hydrobasaluminite
hydrobiotite
hydrocerussite
hydrohetaerolite
hydrokenoralstonite
hydrozincite
“illite”
ilmenite
ilsemannite?
iodargyrite
jacobsite
jalpaite
jarosite
johannite
jôkokuite
kaolinite
kësterite
kettnerite
kiddcreekite
kornelite
kostovite
krennerite
krupkaite
ktenasite
kuramite
langite
laumontite
leadhillite
lepidocrocite
“*lepidolite*”
likasite
lime
linarite
liroconite
litharge
luzonite
magnesite
magnetite
malachite
manganite

matildite
mawsonite
meionite
melanterite
melonite
metavoltine
microcline
miersite
mimetite
minium
molybdenite
mottramite
murdochite
muscovite
nambite
nantokite
natrolite
nekrasovite
neltnerite
nolanite
nordstrandite
“*oligoclase*”
opal
orthoclase
osarizawaite
paracoquimbite
paramelaconite
paratacamite
paratellurite
pearceite
pectolite
petzite
pharmacosiderite
phosgenite
pickeringite
“plagioclase”
planchéite
plattnerite
plumbojarosite
polybasite
powellite
prehnite
pseudomalachite
pumpellyite
pyrargyrite
pyrite
pyrolusite
pyromorphite
pyrope
pyrophyllite
pyrrhotite
quartz
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ransomite
rhodochrosite
rhodonite
rhodostannite
rhomboclase
rickardite
romanèchite
römerite
roquesite
rosasite
roscoelite
rozenite
rucklidgeite

scheelite
schorl
scorodite
scorzalite
sengierite
sepiolite
shattuckite
siderite
siderotil
silver
smithsonite
spangolite
spertiniite
spessertine
sphalerite
spionkopite
stannite
stannoidite
stevensite?
Stibiconite?
stibnite
stolzite
stromeyerite
stützite
sulfur
sylvanite
szomolnokite
talc
tangeite
teineite
tellurite
tellurium
tellurobismuthite
tennantite
tenorite
tetradymite
tetrahedrite
thomsonite
tilasite
titanite
tolbachite
torbernite
tremolite
tungstenite
turquoise
tyrolite
tyuyamunite
uraninite
uranopilite
vanadinite
variscite
velikite
vesuvianite
volborthite
volkonskoite
voltaite
volynskite
willemite
wittichenite
"wolframite"
wollastonite
wulfenite
yarrowite
zincobotryogen
zincocopiapite
zippeite

Table 7: List of the mineral species recognized at Bisbee, Arizona

Those noted in *italics* indicate that the species is no longer considered valid, while a? indicates a questionable status as a valid species, while ¿? is used where the species may be man-made. These are included to allow for referencing the historical identification in earlier studies by those who have studied Bisbee in the past.

MINERALIZATION

From an economic mineral deposit perspective, it all began with a multi-stage intrusion and accompanying mineralization ~ 200 million years ago (Ma), (Lang, 2001). The initial phase of silica-iron-sulfur mineralization followed the emplacement of the first of the several intrusive units into the surrounding country rock flanking the Dividend Fault for a distance of two-plus kilometers along its strike. This was the beginning of the Sacramento Stock Complex, with several subsequent intrusions and a large intrusion breccia interspersed with several episodes of mineralization. It was the centroid of the intrusions and mineralization.

Immense amounts of pyrite were deposited, both as huge manto and, less often, chimney-type carbonate replacement deposits in the sediments and the basement unit, as well as large amounts of disseminated pyrite in the first intrusive unit. The Older Porphyry unit was silicified, as were large areas within the hosting sediments and meta-sediments. Localized intense fracturing and brecciation, as ground preparation, must have occurred prior to the injection of the copper-bearing solutions (Bryant and Metz, 1966).

Further, Bryant and Metz (1966) estimated that in excess of 500 million tons of pyrite were emplaced during this phase. Vast amounts of early-stage pyrite-silica were deposited stratigraphically below what became the locus of the economic orebodies. The later copper-bearing solutions were forced through these now nonreactive lower pyrite deposits to the reactive limestone beds above (Bryant and Metz, 1966). These pyrite deposits were found under the large orebodies at the Cole, Shattuck, Irish Mag, Lowell, and Oliver zones. Early silicious pyrite was found below the massive Campbell orebody. Other areas in the Campbell area showed similar deposits but less intense (Bryant and Metz, 1966).

Subsequently, there was an iron/copper mineralizing event, which followed the dikes and other structures, often replacing parts of the earlier pyrite deposits. Many sulfide copper deposits were emplaced around the periphery of earlier pyrite bodies; indeed, there were few exceptions. It was quite common to find important orebodies within the pyrite masses. Nye (1968) noted that *"Copper sulfides replaced, or partly replaced, individual shattered grains and aggregates of pyrite as disseminated deposits in selected localities controlled by fracturing, surrounded by large areas of disseminated and bedded pyrite containing only trace amounts of copper."*

This event created the many hundreds of copper/iron sulfide carbonate replacement deposits in the limestones, as well as depositing significant copper in the Younger Porphyry unit of the Sacramento Stock Complex. These were to become the ores that were mined at Bisbee for so many years. It is possible that this phase was coincidental with the emplacement of the intrusive breccias (Bryant, 1974), but this is not certain.

The third mineralizing episode was a lead/zinc phase, bringing large manto (flat-lying, bedding controlled) and, less often, chimney-type sulfide carbonate replacement-type deposits in the limestone. This event did not mineralize any of the intrusive units. In many areas, these lead and/or zinc ores were emplaced adjacent to some of the preexisting pyrite and pyrite/copper sulfide replacement deposits, but in general, they were more distal. Schumer (2017) suggests that in many cases, these were largely just re-mobilized and redeposited a bit farther from the centroid of mineralization. There is substantial evidence to support this position.

Though minor in importance when compared to the copper deposits, the lead/zinc deposits played a vital role in the overall economic success of the mines at Bisbee. There were also, several periods when the lead/zinc supergene ores were mind, notably at the Shattuck Mine. The hypogene lead/zinc ores in the Campbell, Junction and Denn mines kept Bisbee operating just after World War II. The copper market had been hit hard by the many thousands of tons of salvaged brass artillery shell casings brought back from Europe and the South Pacific. That sent the price of copper to relative lows never before seen. Even the penny coin was made from shell casings for several years. Also, the lead/zinc minerals and their associated gangue minerals added an interesting dimension to the mineral suites deposited here, as demonstrated by the post-1980 new finds.

Lastly, a multi-element phase was imprinted over the iron/copper-lead/zinc sulfide replacement deposits (Graeme, 1993). Excepting the Sacramento Stock Complex, it was district-wide. In reality, there may have been several pulses of variable chemistry, but the results were identical. While the total volume of mineralization associated with this apparent final phase was very small, it was relatively rich in precious metals and, therefore, economically significant.

Anomalous amounts of antimony, arsenic, tin, bismuth, vanadium, tungsten, gold, silver, tellurium, and uranium were also present in these mineralizing fluids, making the products of this episode mineralogically quite diverse, allowing the formation of scores of interesting hypogene minerals. The presence of unexpected elements bismuth, cobalt, indium, and nickel were first noted by Burnham (1955), but nothing new for Bisbee's mineralogy was confirmed. It was the advent of much-improved detection equipment that allowed sense to be made of these extraneous elements most of 30 years later.

Alan Criddle and Chris Stanley, both of the Natural History Museum in London, conducted an extensive study of ores from the Campbell mine for Phelps Dodge (A. Criddle, personal communication, 1992). These specimens were mainly from the remaining pyrite shell of the Campbell orebody and were associated with high precious metal content (Phelps Dodge, personal communication, 1983). Independently, Sidney Williams, head of the Phelps Dodge Research Laboratory, also investigated many of these same ores as well as materials from several other mines (S. Williams, personal communication, 1992).

The results of both studies were very similar; a previously unrecognized, late-stage, multi-element mineralizing episode had occurred district-wide, excepting the intrusive units. This event resulted in the formation of a broad suite of minerals, often in complex assemblages but always in very minor amounts (Graeme, 1993). For the most part, these minor accessory minerals contain gold, silver, bismuth, tellurium, tin, tungsten, uranium, and/or vanadium. They occurred as combinations of one or more of these elements along with the economically important elements: copper, zinc, lead, gold, and silver. However interesting these species are, they are never seen as crystals, but only in polished sections (A, Criddle, personal communication, 1992) and are very much overshadowed by the common hypogene ore minerals such as chalcopyrite, bornite, chalcocite, sphalerite, and galena.

Our position that the last two mineralizing phases was district-wide, excepting the porphyry intrusives of the Sacramento Stock Complex, is based on two factors. First, using uranium as a proxy for the whole of the mineralizing suite of these elements allows for the ready determination of the presence of these elements by measuring radioactivity. Wallace (1956) studied the relationship between uranium and the hypogene ores, noting: *"The disseminated ore* [pit ores] *exhibits no anomalous radioactivity, and samples from the Lavender pit contain from 0.002 to less than 0.001 percent equivalent uranium. The limestone replacement ores are distinctly radioactive, and stoping areas can be readily distinguished from unmineralized ground on the basis of radioactivity alone. The equivalent uranium content of the copper replacement ores ranges from 0.002 to 0.014 percent, and averages about 0.005 percent; the lead ~ zinc replacement ores average more than 0.007 percent-equivalent uranium."*

Secondly, a review of hundreds of assay determinations of both the mill concentrates and rarely tails show but a trace of lead or zinc. These analyses were important in determining the quality of the concentrates, as zinc is an unwelcome contaminate in a copper smelter.

As an aside, in the 1980s, Phelps Dodge sought permission to recover uranium from the same solutions that copper was being recovered. Something which had been done for decades. The request was overwhelmingly denied. While we cannot comment from an informed position, we believe the word "uranium" was too politically charged to accept such a recovery plant.

This multi-mineral phase seems to have been somewhat uneven in the emplacement of the minerals formed during this episode. Close examination of sulfide hand specimens shows varying intensity and diversity of deposition of the odd species formed over the space of several meters or less.

Because of the difficulty in finding and identifying these unusual species deposited in the earlier sulfides, few clues to their distribution are to be had. As we have previously published (Graeme, 1993), there appears to be a relationship between the vertically zoned matrix mineralogy of several of the limestone rock units and the elements deposited. Only the Campbell orebody was studied sufficiently to make this very general assumption that the matrix mineralogy in the different lithologies was possibly an important determining factor. Criddle noted that the matrix mineralogy at the 1600 level (Naco limestone) was largely siliceous hematite; the 2100 level (Escabrosa limestone) was predominately pyrite/calcite, and the 2566 level (Martin limestone) graded into a pyrite/calcite/ quartz

Interestingly, in spite of the enormous volumes of sulfide minerals deposited at Bisbee, crystals of the sulfide minerals are uncommon, and truly good specimens of sulfide species are relatively rare, if any, exist. These massive sulfide replacement deposits were very tight and compact with very few voids, reflecting the nature of the replaced limestones. In many cases, the replacement of the limestone was quite faithful to the point of preserving textures and even minor features such as fossils. Criddle (personal communication, 1992) said that in the hundreds of specimens studied, not a single crystal was seen without magnification. There is absolutely no evidence of any open space deposition by sulfides in the limestones (Bonillas et al. 1916). Thus, there were few opportunities for crystal growth.

Post-mineral, hydrothermally developed voids were relatively common in the eastern edge of the district. These were usually near large lead/zinc replacement deposits but not related to the lead/zinc and totally devoid of sulfide mineral crystals. Most such openings were lined with hydrothermal goethite and/or pulverulent manganese oxides calcite. The calcite is invariably fluorescent and often formed fine mineral specimens.

The depth at which mineralization took place appears to have been relatively shallow. Nye (1968) suggested this. His supposition is strongly supported by the subsequent recognition of the Lowell volcanics sitting on the deeply eroded Paleozoic sediments adjacent to the Sacramento Stock Complex. Using the Glance Conglomerate - Paleozoic limestone contact in the close-by Junction shaft as a marker, mineralization took place less than 50 meters from the Jurassic surface in some places. The lower extent of mineralization is uncertain. A vertical drill hole in the east-most part of the 3200-level drilled in 1974 bottomed in mineralized Pinal schist with abundant pyrite at 120 meters for a vertical extent of at least 750 meters below the pre-Cretaceous surface.

During the early 1970s, in a radon gas study, one of the authors (RWG III) took hundreds of readings in the east and southern parts of the productive area with scintillation and Geiger counters. Later the authors conducted a similar, though less intense, review of the western part. Both studies confirmed Wallace's conclusions. Also, the presence of various supergene minerals containing one or more of the anomalous elements has been confirmed district-wide, indicating the presence of several elements. Vanadium secondary minerals were the most common.

Further, the wide distribution of important amounts of both gold and silver throughout the replacement ores, all of which contained significant precious metals, while little if any gold and silver were found in the intrusive ores, support this thesis. We have taken and analyzed thousands of samples underground and reviewed the assay reports, most as a normal part of the work as a geologist. Few were the gold assays of less than 0.15 ounces per ton and 2 ounces per ton for silver. Historical records reflected this trend as consistent over the life of the mines and held true for both oxide and sulfide ores. This correlation is not a coincidence. The last phase of mineralization was district-wide, but, as previously noted, it did not affect the intrusive hosted ores,

PARAGENESES:

Over the last century, a number of very capable workers made honest efforts to unravel the complex paragenetic sequence of the complex mineralogy at Bisbee. Each was restrained by the data available, something that evolved over time as more areas were opened, notably to the east and south of the Sacramento Stock Complex.

Ransome (1904) saw little of the hypogene sulfide mineralization and expressed doubt the sulfides were an important feature of Bisbee’s future. Tenney, in 1914, was the first to postulate an ordered sequence of pyrite – sphalerite – galena – bornite. He did not speculate on the number of mineralizing events. In 1932, Schwartz and Park, in a quite detailed study of the Campbell area, saw more than a single mineralizing event and that what they had found was definitely a somewhat different sequence. They saw pyrite – chalcopyrite – bornite – chalcocite – sphalerite – galena.

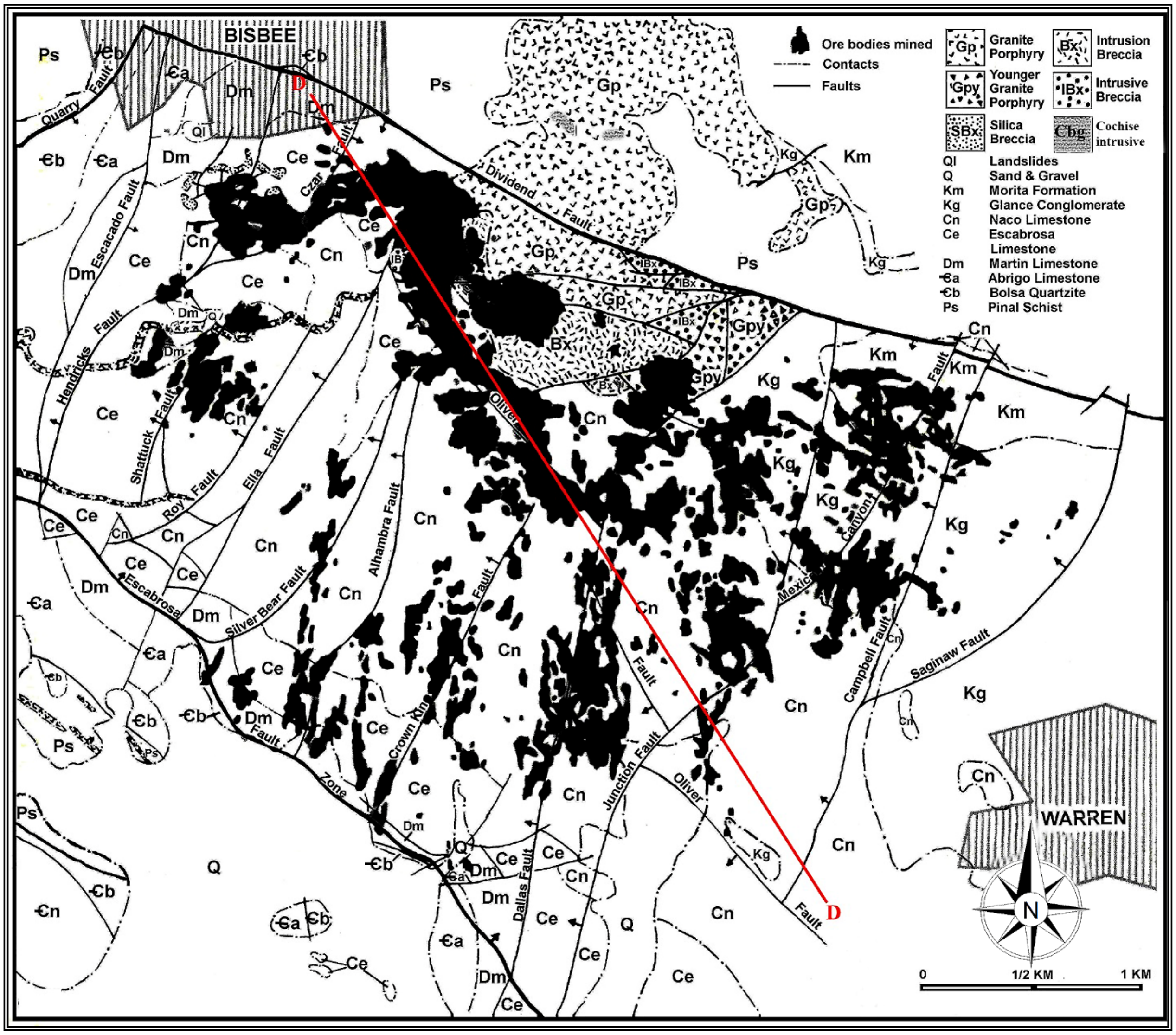
Bryant and Metz (1966) took a different view of the mineralization sequence. They proposed that, first, enormous amounts of massive silicious pyrite with minor copper content were deposited. This was followed by localized, structurally controlled copper mineralization consisting of chalcopyrite, bornite, chalcocite, and pyrite. Following this was an episode of lead and zinc mineralization.

Our first overview in 1981 (Graeme, 1981) recognized multiple mineralizing events with the following sequence: pyrite – galena, overlapping with sphalerite; then a chalcopyrite/pyrite event merging into partially overlapping bornite/chalcocite, which was followed by sphalerite/galena. It was a typically simple and straightforward paragenesis, different from other workers.

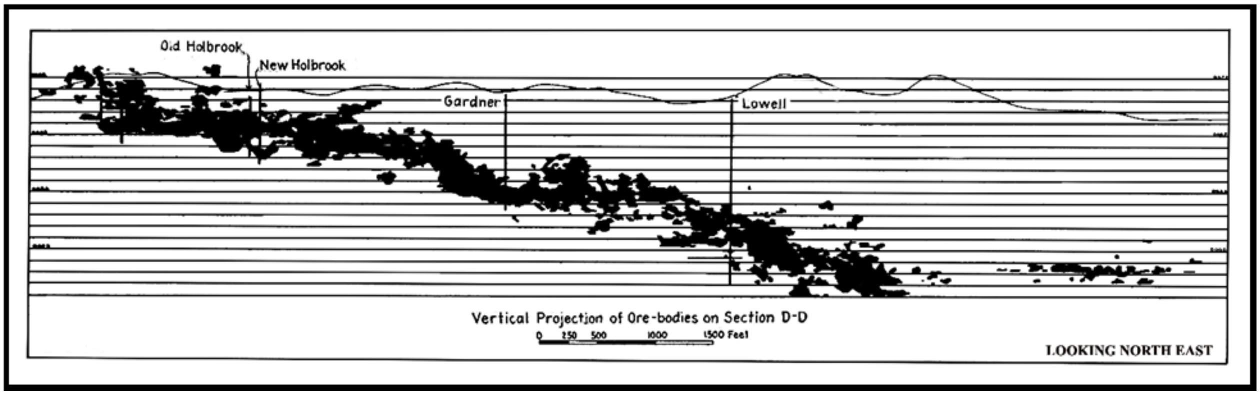
In our 1993 work (Graeme, 1993), we continued to see the same sequence, but the work by Criddle (A. Criddle, personal communication, 1992) and Williams (S. Williams, personal communication, 1992) had shown a late-stage, multi-element event in the Campbell area. However, our fieldwork found more than sufficient evidence to show that this last multi-element mineralizing event was district-wide. As noted below, Schumer found a district-wide distribution of the uncommon elements as well.

Schumer (2017) reviewed the paragenetic relationships, mineral chemistry, and zoning of the complex and diverse ores and concluded that oxidized magmatic-hydrothermal fluids were responsible for mineralization at temperatures between 325ºC and 450º C. Schumer divided the ores into chalcopyrite-rich, bornite-rich, and chalcocite-rich types.

Quoting Schumer (2017): *"Chalcopyrite-rich ores contain the assemblage chalcopyrite + chlorite + quartz ±pyrite associated with lesser hematite, magnetite, and anhydrite, with accessory minerals dominated by Bi-sulfosalts or sulfotellurides and minor uraninite, scheelite, or cassiterite. Tellurides occur in chalcopyrite + pyrite assemblages in deep levels of the Campbell and Higgins mines. Bornite-rich ore is dominated by the assemblage bornite + pyrite + muscovite and contains accessory tennantite and Cu-Sn-V-W sulfides. Chalcocite-rich ore is composed of three assemblages: digenite-chalcocite + pyrite + kaolinite-dickite + quartz, enargite or luzonite + pyrite+ quartz, and covellite + kaolinite-dickite + quartz. Zinc-lead ores are composed of the association sphalerite, galena, quartz, pyrite, tennantite-tetrahedrite, chlorite and/or lesser siderite."*

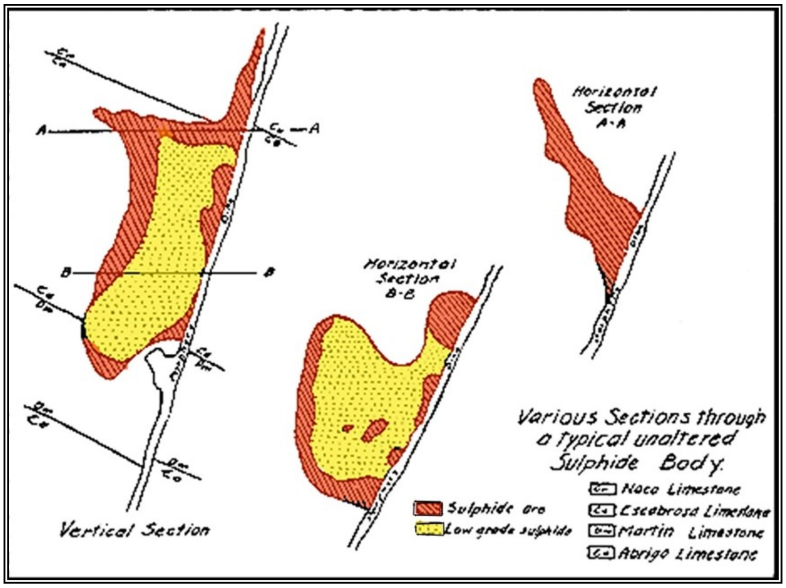


General geology and horizontal projection of ore mined underground through 1975. (after Graeme, 1981)



A projection of ores within 150 meters of section D-D as of 1916, after Bonillas, et al. (1916). While substantial ore was mined post-1916, the trend of the southeast dip continued.

REPLACEMENT DEPOSITS:



A generalized sketch of what Trischka (1938) presented as" various sections through a typical unaltered sulfide body."

The sulfide carbonate replacement deposits that resulted from the mineralization are generally arranged around the Sacramento Stock Complex in a semicircular fashion, with offshoots radiating outward like the spokes of a wheel. This arrangement is the result of orebody concentrations in and along fractures and fault zones (Bryant & Metz, 1966). The crescent-like arrangement of the ores is a reflection of the shattered zone in the limestones (intrusion breccia), which surround the southern portion of the stock complex, while the "spokes" reflect the fault zones and fractured areas (Bonillas et al. 1916), (Bryant & Metz, 1966), (Nye, 1968). They are continuous for a distance of up to four kilometers, becoming deeper to the southeast, mainly due to post-ore covering and tilting, which add more than 500 meters vertical distance. In all, the ores had a vertical extent of ± 1300 meters (Nye, 1968).

As noted by Nye (1968), the replacement of the earlier pyrite by copper minerals was generally uneven. Locally, ore occurs along the margins of massive pyrite deposits and adjacent to crosscutting fractures within these deposits (Nye, 1968), as shown in the above illustration from Trischka (1938). The many carbonate sulfide replacement masses deposited in the limestones were deposited as mantos in the Martin and Abrigo limestones and as chimney forms in both the Escabrosa and Naco units. The massive sulfides were usually deposited as faithful replacements of the hosting limestones. The sulfide replacement was often quite faithful, preserving features and characteristics of the limestone on a macro level. In one massive bornite/chalcocite/pyrite stope on the 2700 level Campbell, almost every feature of the limestone had been preserved with a chert bed passing from clean limestone to altered limestone through the massive sulfide and grading into altered, then clean limestone some 15 meters distant. Many other such deposits at Bisbee manifested the nature of the now replaced limestone, and even silicified fossils were frequently preserved.

These deposits were often huge, with the sulfides deposited in many hundreds of usually isolated masses, varying in size from thousands of tons to a few million tons. They were scattered in the hosting limestones and seldom connected, even by structure. This feature greatly complicated exploration. The ore component of the individual deposit was quite variable. They were always pyrite dominant, with the pyrite portion usually several to many times the volume of the ore minerals.

Economic orebody sizes were quite variable. Metz (1956) estimated that one-third of the ore production came from orebodies less than 10,000 tons, another third from ore masses of 10,000 to 25,000 tons, and the remainder with total ore tonnages over 25,000 tons. There were several very large deposits, with a few copper orebodies exceeding one million tons of minable ore (Bryant & Metz, 1966). Examples include the Campbell orebody and the thoroughly oxidized Atlanta, Southwest, and New Southwest orebodies. This is ore tonnage only, with the associated gangue minerals, usually pyrite, several times the size of the ore tonnage. Some pyrite masses with little to no economic value were found as well, but these were uncommon.

No two of the replacement deposits were identical, similar, yes, identical, no. This RWG III learned from looking at a new face of blasted ore or pulling the fresh ore from the chutes six days a week for 12 years. Then some three years as a geologist, mapping, studying the ores, and searching for more. This taught him to recognize the differences. In general, the sulfide minerals were the same, but there were substantial differences in the relative volumes as well as the manner in which the sulfides were intermixed. There were distinct differences in each orebody, with copper content varying in the space of a meter or less. The same was true for gold and silver as well as the included uncommon, multielement species. With the latter group, changes in the overall mineralogy occurred over a distance of just several centimeters, and typically, no two hand specimens were truly identical.

A freshly blasted sulfide muck pile of the intrusion breccia in the Sacramento Mine. The timber to the center-left has numbers written with chalk indicating the copper grade for the material mined behind the post – 3.0% first and then 2.8%; both below ore-grade. The size and number of boulders present tells of hard rock; rock that must be broken by hand to pass through the rock handling system. Photo circa 1918 Graeme-Larkin collection.

The varying mineralogy and copper grade required that every round (material blasted in a shift) of two-plus meters in length had to be sampled and assayed. Every day, the assay lab would run several thousand determinations for copper, gold, and silver as well as lead and zinc, if requested by the sampler.

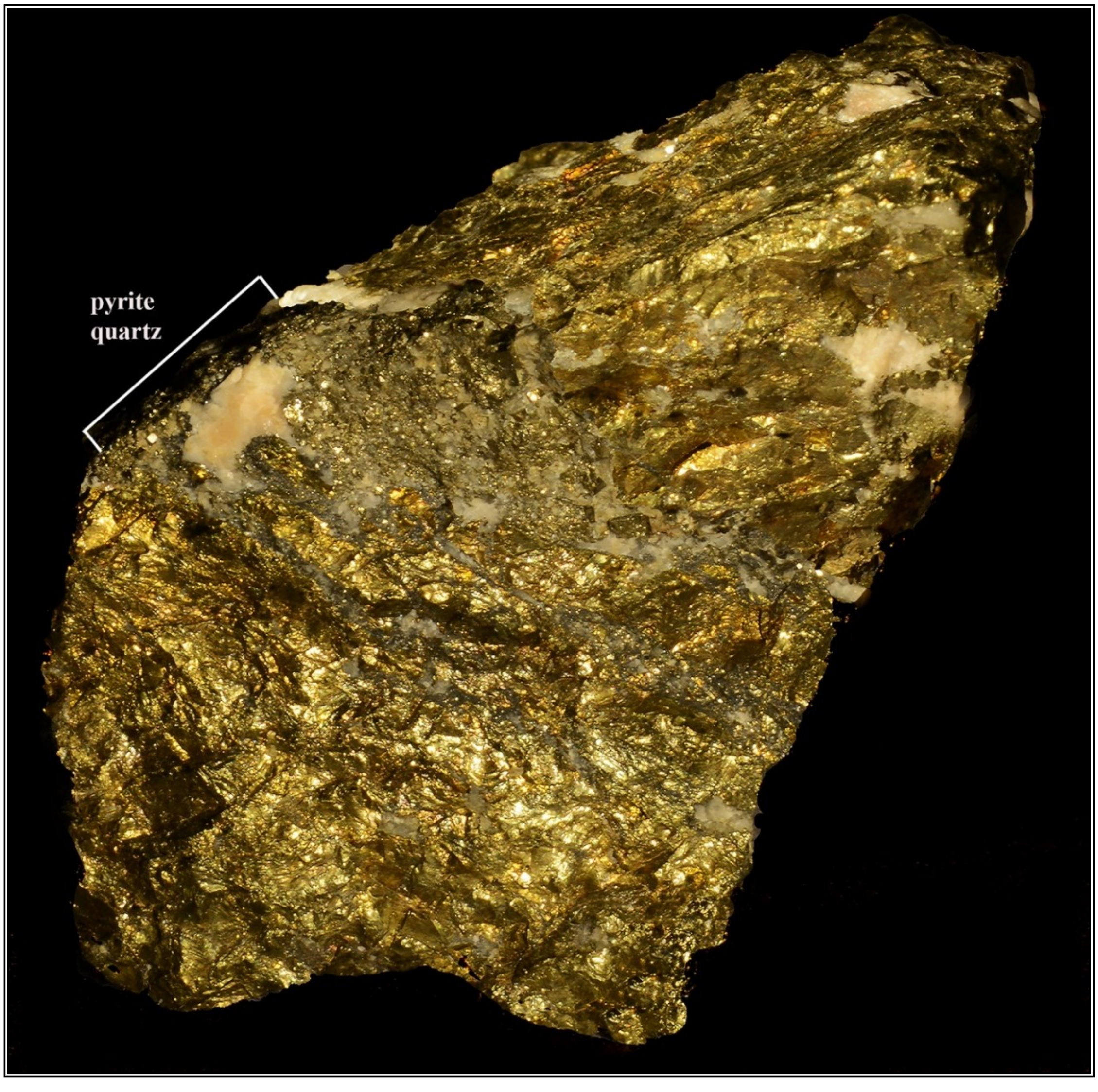
For the most part, the replacement bodies were a complete replacement, though irregular in shape and near-pure sulfides mixed with minor amounts of hydrothermal gangue minerals such as quartz and calcite as minor inclusions and veinlets. The occasional small mass of unreplaced limestone encased in the ore was found during mining. These could be up to several meters in size.

In general, the rock quality surrounding the sulfide carbonate replacement deposits was excellent, as seen in the below photograph, where the sulfides were usually extremely competent. Little if any support timber was ever needed, and the timber that was installed was usually for keeping the ore separated from the waste during mining, controlling backfill, and in the lining of raises for ore handling.

Drilling a blast hole with a jackleg drill in a massive sulfide stope. The minerals are a mix of bornite (lower-1/3), chalcopyrite (left and below of drilling point), pyrite (upper-right corner). The black sludge coming from the drill hole is typical, as all sulfides yield black powder when finely broken. 2833 level, Campbell Mine. The ore from this blast ran 5.8 percent copper. Peter Kresan photo, 1974.

The visual sense of standing in a large open space with nothing but golden-yellow chalcopyrite/pyrite, pinkish to purple bornite, and gray chalcocite, often streaked with silver-gray tetrahedrite, all surrounding you was stunning – the sheer volume of sulfides was always visually overwhelming. Words are inadequate to describe the sensation. Even though acceptable mining practices required gobbing (backfilling), huge openings in relatively fresh sulfides could be developed before being gobbing. As a point of interest, sulfide-bearing waste could not be used for gobbing due to the fire risk associated with the exothermic decomposition of sulfides.

While the massive sulfide bodies were most often compact and well-indurated, some large pyrite masses were crumbly, even sand-like, though very rarely ore grade. These were difficult to mine, as controlling flow of the sandy material required that even the smallest hole in the timber be well plugged, or the pyrite would flow into the work area. The miners hated this type of pyrite occurrence and call it "sugar sulfide," as it ran like granular sugar. And too, the small particle size allowed the pyrite to oxidize rapidly, generating sufficient heat to ignite the timber, if not controlled by adequate ventilation. The working environment was horribly hot, and the sulfide dust burned the nose and throat terribly. Thankfully, these deposits were rare.



Chalcopyrite with an irregular vein of pyrite and quartz, very much like the chalcopyrite shown in the stope photograph before. The pyrite veinlet was intruded into the massive chalcopyrite. Campbell Mine. Specimen 11 cm. Graeme collection.

In spite of their relatively large size, finding these deposits was a daunting challenge. The favorable indicators – structure – intrusive dike – intrusive breccias – hydrothermal alteration were far more pervasive than the ores. As little as a meter of alteration may surround a substantial sulfide replacement deposit with silicification, pyritization, and recrystallization or a combination of any or all present. In many instances, the sulfides were in direct contact with the limestone with no evident alteration.

Exploration was ever challenging. In the last dozen or so years of operation, some 14 diamond drills were continually employed in the search for ore. Yet, seldom were there ever more than two years of minable reserves on the books. You never knew when you were close to ore. More than a few good geologists were humbled while searching for ore at Bisbee (including one of the authors).

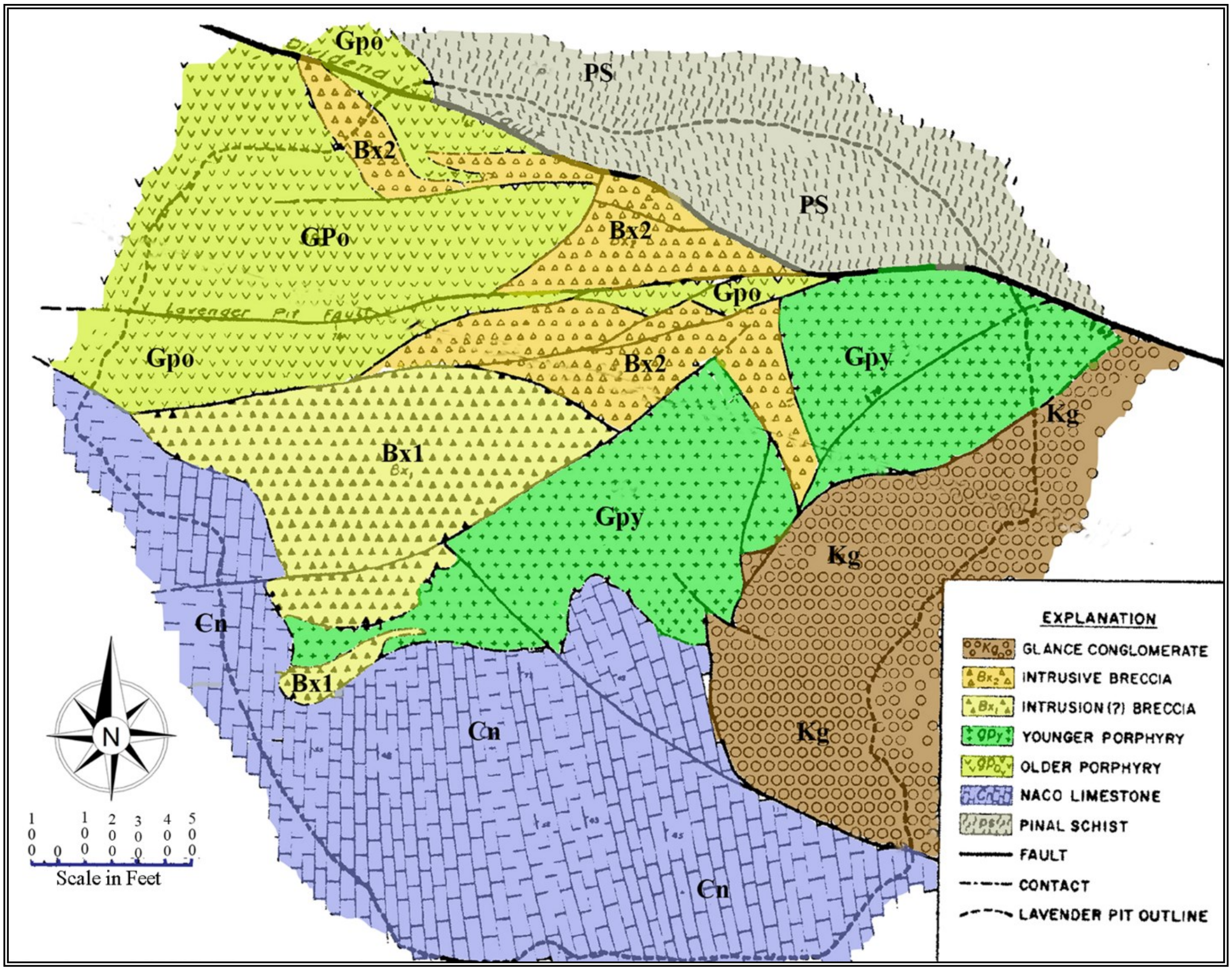
On a micro-scale, these were massive, fine-grained deposits with very, very few voids, except for usually small, preexisting cracks. The grain size was most often tiny, with 0.5-0.1 mm not uncommon. This is why so very few sulfide mineral crystals have been found at Bisbee – no open spaces for them to develop. As other species were always present in the copper sulfides, such as intermixed pyrite and/or other ore minerals, masses of pure chalcopyrite, bornite, or chalcocite any size were uncommon. Close examination of seemingly pure chalcopyrite, bornite, or chalcocite would show included quartz, pyrite, and/or other minerals.

Recent work by Alan Criddle, Sid Williams, and Ben Schumer have identified a host of rare and unusual hypogene species with gold, silver, tin, bismuth, vanadium, tungsten, arsenic, antimony, and tellurium as intergrowths/replacements in the more common copper sulfide ore minerals from the Campbell, Dallas, Cole, and Southwest mines. However, the presence of some or most of these same elements in the secondary mineral suites in the Dallas, Holbrook, Shattuck, Czar, and Higgins mines indicates that the multi-element mineralization episode was indeed a district-wide event; excepting the intrusive of the Sacramento Stock Complex.

Zinc and lead ores were common throughout the district and were economically significant during several periods of Bisbee's mining history. An economic cut-off grade of 20 percent of the combined metals was employed during the 1940s (Mills, 1958). The occurrence of the zinc/lead ores was similar to the copper deposits. Bodies rich in sphalerite and galena with abundant accessory pyrite and quartz were widespread, usually distal to the copper deposit. These, too, were direct replacements of limestones. The most common minerals were sphalerite, galena, and the ubiquitous pyrite, with minor amounts of chalcopyrite. Schumer (2017) noted alabandite, and rarely tennantite-tetrahedrite, with quartz, calcite, siderite, and rhodochrosite as the more common associated minerals.

SACRAMENTO STOCK COMPLEX MINERALIZATION:

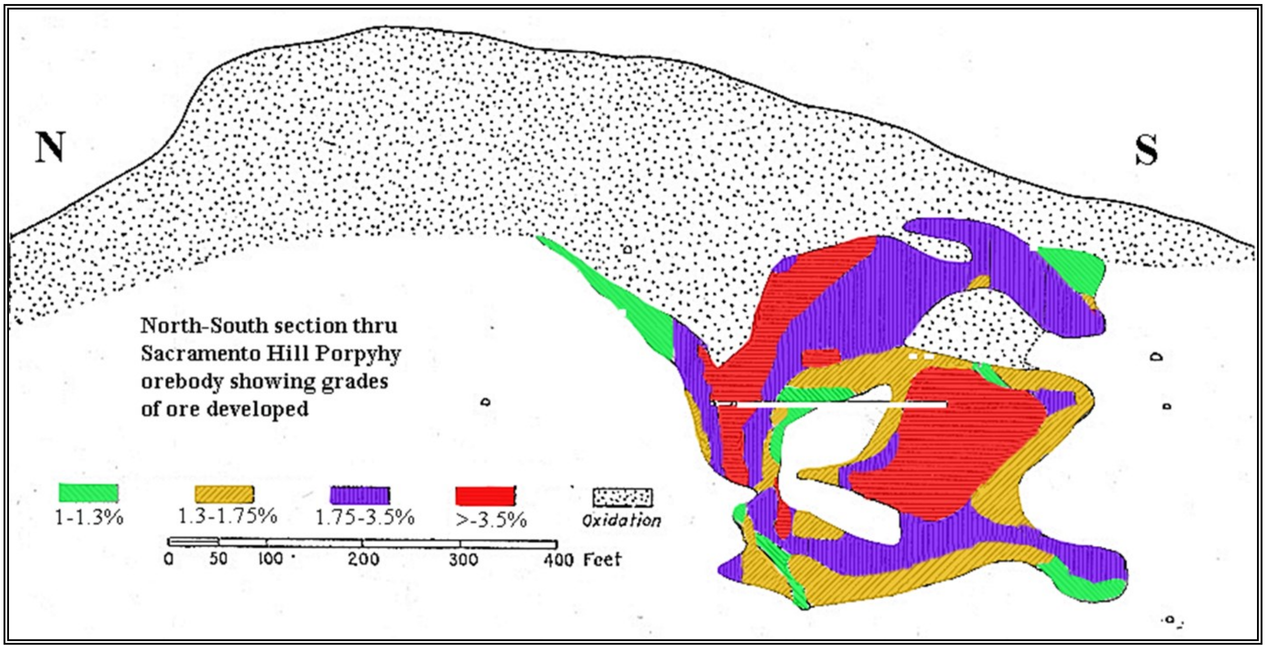
From a miner's perspective, the Sacramento Stock Complex hosted a small, medium-grade, but metallurgically difficult copper porphyry. The several intrusive units in the Sacramento Stock Complex were mineralized differently. The Older Porphyry unit was heavily pyritized (15%-18%), silicified, and virtually rendered impermeable to the subsequent copper-bearing fluids. Thus, it contained few hypogene ore minerals except for a small, highly fractured area in the southwestern part of the Lavender Pit, where a few high-grade spots were mined (Bryant &



Surface geology of the area to be mined by the Lavender Pit, with the proposed pit outline. The faulted and jumbled and intertwined nature of the intrusives units and breccias are why we refer to it as the: Sacramento Stock Complex. Only the Younger porphyry, the Intrusion breccia and the Intrusive breccias contained significant ore grade material of note (> 0.35% Cu); very minor, localized amounts of ore were found in the Older porphyry. After Bryant and Metz (1966)

Metz, 1966). Much of Sacramento Hill was composed of this Older Porphyry unit. It remained as a largely unmined, gossan-capped knob along the northern side of the Lavender Pit.
On a bench-level blasting (bank shot) scale, 15 m X 50-75 m; the ore-leach-waste relationship was even more complex. Bryant and Mets (1966) noted, *"Even in the ore area, there is seldom a bank shot that does not contain ore, leach-ore, and waste. Careful, selective mining is necessary and is made possible with truck haulage* [as opposed to rail haulage] *and blast-hole control samples."* A detailed review of "leach ore can be found in volume III of this series.

Vertically, the complexity of the intra-rock type relationship was perhaps even more complex. Supergene enrichment had followed the many faults during the several supergene episodes, completely leaching copper from the gossans. The complexity by grade is illustrated in the below cross-section, with supergene enrichment the dominant variable and rock-type the second most important factor.



A very generalized cross section thru Sacramento Hill looking east. The indicated ore areas, (> 1% Cu) were mined by the Sacramento Pit. After DeKalb, 1928.

The remnants of Sacramento Hill looking east, as it appeared in 1975, showing high sulfide mineralization in the remaining Older Porphyry and the completely leached gossan. Note the Dividend Fault zone at the left.

Photo closely reflects the cross section above with the ore removed by the Sacramento Pit. Graeme/Larkin collection.

In the Younger Porphyry unit, mineralization was erratic and relatively low grade. It consisted of minor amounts of chalcopyrite and bornite associated with abundant pyrite in a disseminated fashion, as is typical of copper porphyries. The several periods of supergene alteration added the typical "chalcocite blanket" to parts of this porphyry unit as chalcocite coatings on pyrite and made it economical with open pit mining and flotation recovery. Neither the lead/zinc mineralization nor the last phase of mineralization, rich in anomalous elements and precious metals, appear to have mineralized this area.

The Intrusive breccia associated with this complex was mineralized in a more or less disseminated manner with chalcopyrite and bornite and tiny amounts of sphalerite and galena present. This was the only part of the Complex that contained any lead or zinc and, for the most part, it appears to have been within the breccia when emplaced. Bryant (1974) has suggested that this breccia may well have been sulfide-bearing at the time of intrusion, something with which we agree.

One of the most economically important units was the intrusion breccia. It was the source of substantial amounts of high-grade ore for the Gardner and Sacramento mines as well as both open pits. This unit had a matrix of siliceous rock flour and locally, sulfides, with brecciated fragments of the various rock units, many of which were replaced by sulfide ore minerals. The clasts were often large and entirely replaced by hypogene ore minerals making very rich ores. Interestingly, little of the intrusion breccia was oxidized, no doubt due to the intense silicification, which protected the sulfides.

The Warren porphyry, located underneath both the Older and Younger porphyries, contains disseminated chalcopyrite with less pyrite than the Younger porphyry and contains minor molybdenite. No other porphyry unit at Bisbee contains anything more than localized traces of molybdenite. No evidence of any supergene enrichment in this deep porphyry was noted. This modest mineralization never approached economic levels of metal content.

The Cochise porphyry was weakly mineralized with disseminated pyrite and lesser amounts of chalcopyrite. Drilling in 1980 confirmed the presence of a chalcocite blanket of variable thickness. This enriched zone was shown to mimic the current topography, merging into the Lavender Pit ores (Cook, 1994). Supergene mineralization includes the replacement and/or coating of pyrite, chalcopyrite, and very minor sphalerite, with chalcocite. Locally, zones of this porphyry unit may become economical as a result of supergene enrichment.

MANGANESE DEPOSITS:

In addition to the copper, lead, zinc, and precious metal mineralization noted above, the limestones at Bisbee also hosted a number of small, isolated manganese deposits. Without exception, these are near-surface deposits containing manganese as one of its several oxides, largely braunite. While mineralogically interesting, these deposits were of economic importance for a very short period of time from 1914 to 1919 to supply the steel alloy metal needs of the First World War.

The time and nature of the emplacement of these deposits are uncertain, but they were probably closely related in time to one of the last phases of mineralization and emplaced as limestone replacement deposits. Factors suggesting a late deposition include; low copper content (Ransome, 1920); the common presence of vanadium (Taber and Schaller, 1930) and arsenic (Palache and Shannon, 1920), (Williams, 1970), and too, their typical, though not absolute association with silica breccias.

All of these deposits occur partially or wholly in limestone in a manner that is highly suggestive of limestone replacement. The contact between the manganese and hosting limestone strongly suggests the replacement of the limestone at the many we have visited. However, there are no known unoxidized equivalents in the district, and no similar deposits have been found

Near-surface manganese stope with the ore zone indicated, Twilight Claim, Higgins Mine – 1967. Graeme/Larkin collection

underground during the near-century of mining. Thus, it is not possible to say with all certainty that these too are replacement-type deposits or what the source of manganese may have been.

Taber and Schaller (1930) suggested these deposits were replacement in origin and Bonillas et al. (1916) were of the same opinion. Bonillas et al. (1916) also noted that the manganese oxides in these deposits are markedly different from those so commonly associated with the oxidized copper replacement deposits throughout the district.

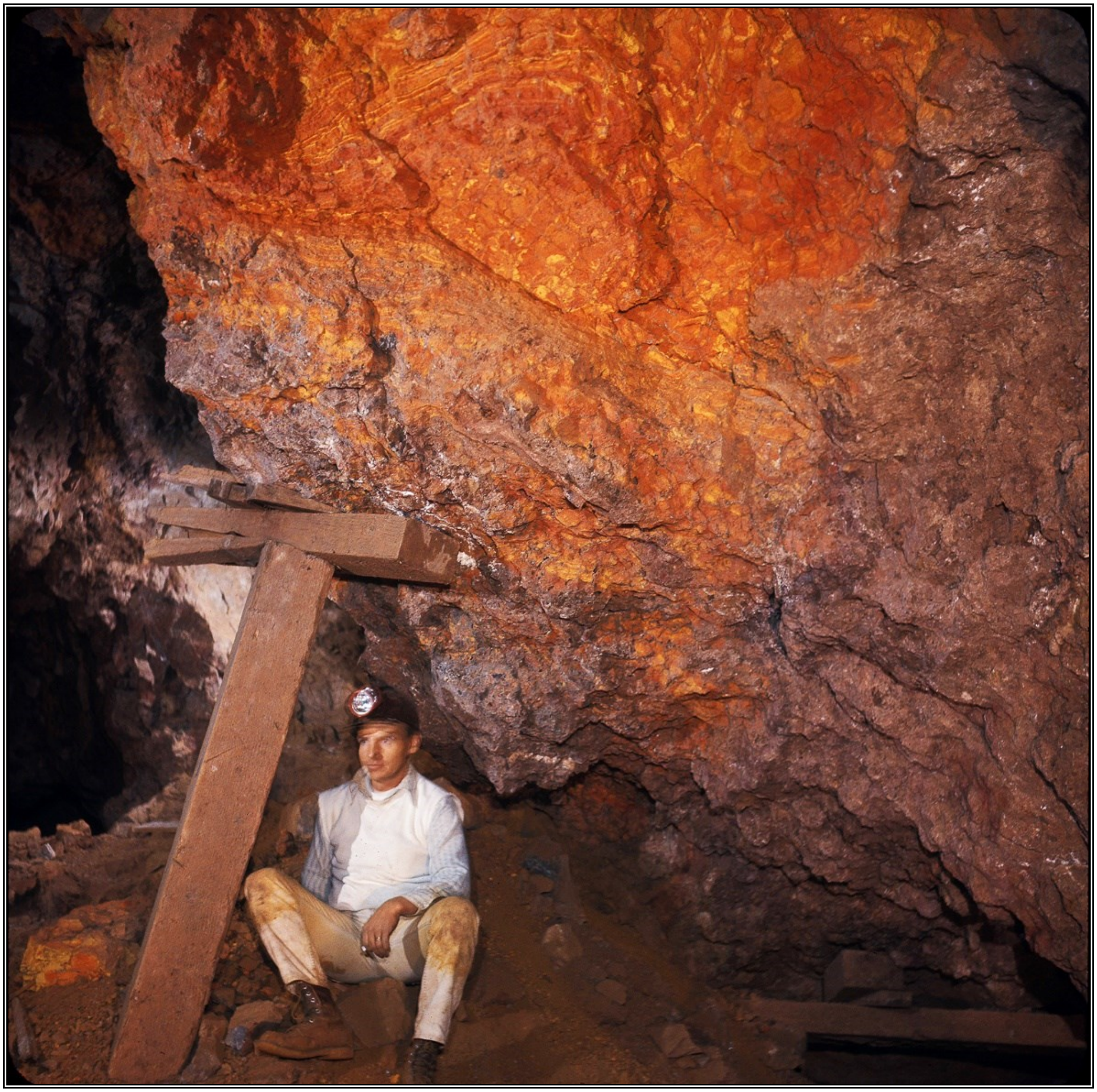
Alabandite, the manganese sulfide, is known from several localities in the district. Tabor and Schaller (1930) studied alabandite in two places in the Higgins mine and suggested this type of occurrence as a possible source for the surface manganese oxides deposits. The two Higgins mine localities have been visited several times by the authors and studied in detail. In both, lead and zinc sulfides were abundantly present, something not seen in any of the many surficial manganese deposits. As previously noted, alabandite was also found in large masses associated with lead/zinc ores in both the Campbell and Junction mines.

A single sizeable underground manganese oxide occurrence on the 1900 level Junction, which was never mined, occurred near lead/zinc orebodies. It has been visited by one of the authors and is very different from the surficial manganese deposits, as it shows typical oxidation features such as boxwork, stalactitic and botryoidal forms. The mineralogy was different, with abundant hetaerolite and minor hemimorphite along with the unidentified pulverate manganese oxides.

That alabandite, which, as noted, was invariably associated with the lead/zinc ores, could have been the source of the manganese in this anomalous deposit is difficult to visualize. Inasmuch as there is very little to no lead or zinc associated with the surface manganese deposits, it suggests that some other type of mineralization must have been the original source for their manganese. In spite of our numerous visits to most of these deposits and countless hours spent reviewing the areas and minerals, the source of the manganese remains uncertain to us. However, we agree with other workers that these are replacements in origin and recent work on manganese deposits elsewhere suggest they could have deposited by the sulfur-poor environment as the oxides and silicates now found (Hewitt and Fleischer, 1960),

SUPERGENE ALTERATION

Supergene alteration, that process whereby hypogene sulfide minerals are altered under near-surface conditions by groundwater and oxygen, aided by bacteria, to generally form soluble sulfates of the metals contained by the original sulfides and redeposited, is well known and understood. Also, the wide variety of minerals that are formed from these solutions, depending on the geologic environment, is equally well documented. Oft times, this process is referred to as supergene enrichment, as the mobilized metals are often concentrated stratigraphically lower in the system. In carbonate-hosted environments, the metals may be redeposited close by, more or less in the same general area if not in-situ through buffering from the carbonates, forming copper, iron, zinc, and lead carbonates, with little, if any enrichment.



Contact between totally oxidized iron oxides and slightly corroded Martin limestone. As this is at the edge of a stope, it would appear that this is a relic of the massive pyrite that so often surrounded copper ores.

The limestone shows some evidence of attack by acidic solutions to a meter from the iron oxide boundary, but is otherwise unaffected by either the hydrothermal solutions or supergene solutions. The horizontally stratified nature of the iron oxides indicates a post-tilting deposition time and thus, it is Pliocene or later in age.

The man in the photo is Al Voirin, one of the very best miners in Bisbee, at the time, and a most discerning mineral collector. Photo taken in 1967. Graeme/Larkin collection.

A number of individuals have studied the geology of supergene copper deposits since the original work by S. F. Emmons (1900) and W. H. Emmons (1913, 1917), which presented their extensive descriptions of enriched ores from a number of the mining districts in the United States. Subsequently, oxidation and the enrichment processes have been studied by many fine geologists over the years. By way of example, Kemp (1900), Stokes (1906), Sato (1960, 1992), Sato and Mooney (1960). Anyone interested in the geology and geochemistry of this process is referred to the authors noted above. What is presented here is but an overview of the recognized events at Bisbee and their distinguishing characteristics.

Later in this volume, several of the more significant aspects of supergene activity as related to Bisbee's supergene mineral development will be explored in more detail. These include oxidation caves, minerals formed in the massive supergene clays, cuprite nodules, and the exotic minerals within, subaerial/subaqueous deposition of azurite and malachite, as well as a look at secondary aluminum minerals and the deposition of chalcoalumite.

SUPERGENE MINERAL PARAGENESIS:

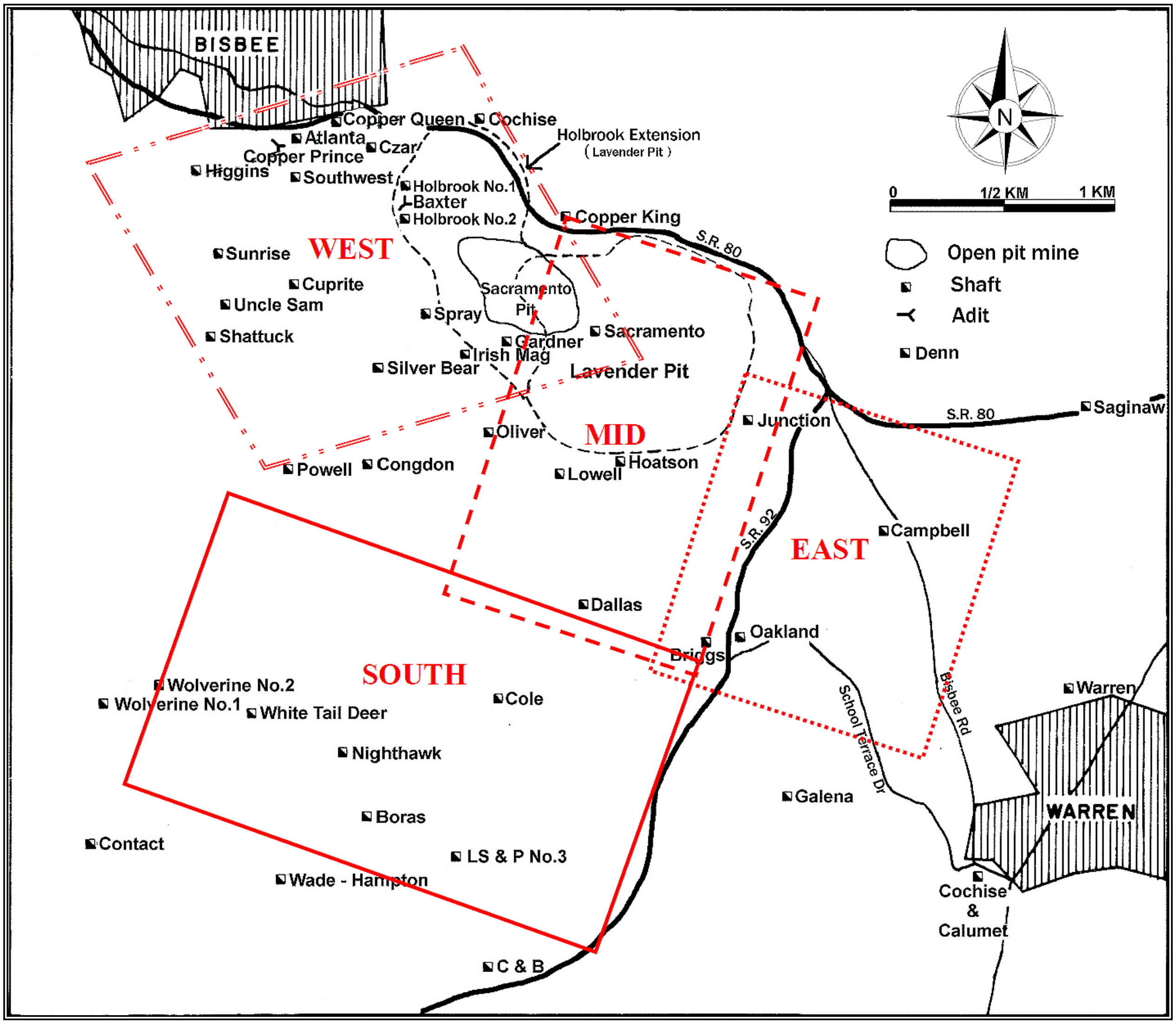
A single, straightforward paragenesis of the supergene mineralogy for the district is impossible to develop. A large number of individual hypogene deposits, their variable copper content, and mineralogy, their relationship to differing host rock units as well as the early supergene gangue minerals derived from the encasing host rocks and the overprinting of subsequent episodes of supergene activity have combined to make the development of a "typical" paragenetic sequence impractical.

To be sure, there are a good many very similar oxidized deposits in the same area of the mineralized zone that could be used to generate a paragenetic sequence of that particular area. However, such a study would reflect this area only and perhaps nearby areas, but little else.

SUPERGENE ALTERATION EPISODES:

While it has long been recognized that there was more than one episode of supergene alteration at Bisbee (Bonillas et al., 1916), an exact number remains elusive. Further, it was not previously recognized that because of an active geologic past that included periods of rapid, high energy erosion, subsequent burial, inundation by shallow seas, regional tectonic events, local movement along the Dividend fault, uplift and localized erosion, different parts of the mineralized area experienced a different number of supergene episodes.

From extensive fieldwork, including thousands of hours underground coupled with the review of literally thousands of specimens, we have recognized four distinct supergene periods in the limestone replacement deposits. That being noted, the eastern part of the district experienced two such events; the mid and southern areas underwent three. The western area experienced all four of the events, with most parts in the west reaching complete maturity in a supergene alteration sense. The last phase of supergene alteration was still ongoing at the time of discovery in 1877.



A very generalized location map of the approximate areas of varying periods of supergene activity, as discussed below. Overlap represents areas where the depth of the individual supergene episodes can be seen as variable and unrelated to previous or subsequent events.

FIRST SUPERGENE EVENT:

Fossil evidence shows that southeastern Arizona was far more humid during the late Jurassic Period than today. Climate, particularly the availability of surface and near-surface water, is a driving factor in the intensity of supergene activity.

The first stage of supergene activity must have occurred in the late Jurassic or very early Cretaceous periods, as clasts of mineralized limestone with gossan, copper oxide, and carbonates with iron and manganese oxides are reasonably abundant in the basal Glance Conglomerate near the Sacramento Stock complex. Also, large fragments of the leached capping from the Complex are included in the conglomerate as well. Stegen et al. (2005) noted that malachite, brochantite, iron and manganese oxides and turquoise are found in the conglomerate, localized in channels along the base of the conglomerate. The matrix is mainly composed of rock flour derived from all of the various lithologies observed in the clasts.

Bonillas et al. (1916) noted that the oxidation in the replacement deposits does not conform closely to the present topography. However, it conforms closely to the pre-Cretaceous unconformity at the base of the Bisbee Group, indicating this first episode of supergene activity occurred while the Paleozoic limestone beds were still largely horizontal. To further confirm that the beds were yet to be tilted when the first supergene activity took place, malachite as stalactitic forms decidedly perpendicular to bedding and not vertical, as related to the orientation of the beds at the time collected, have been found by the authors in the upper-most parts of the Junction and Campbell mines.

The depth of the supergene alteration of this event was quite variable. Oxidized zones were found a few tens of meters below the pre-Cretaceous surface and to 400 meters deep and along strong structures. In addition to azurite and malachite, copper, cuprite, cerussite, and abundant iron and manganese oxides were deposited.

For the most part, the supergene minerals formed during this first event were from a subaqueous environment, as indicated by the high degree of crystallinity present in the deposited azurite. Several areas in the very upper-most parts of the Junction and Campbell mines did, however, contain substantial, local subaerially deposited azurite and malachite. All subaerial deposits from this event were less than 50 meters below the pre-Cretaceous surface.

It is our considered opinion that almost all, if not all of the large, long prismatic crystals (>1 cm) with wedgelike terminations, formally azurite and now malachite pseudomorphs after azurite, were formed at this time. These pseudomorphs, which were found throughout much of the district, were formed in a subaqueous environment and subsequently altered to malachite either in an oxygen-rich subaqueous setting, as manifested by minor contemporaneous malachite deposition. In short, the large azurite crystals formed, followed by district-wide alteration to malachite as part of the first supergene event.

A classic doubly terminated, malachite pseudomorph after azurite. 9 cm. 1300 level Campbell Mine. Graeme collection.

How soon after the azurite crystal formation, the alteration to malachite took place is uncertain, as is the driving force behind such an extensive event. That all of the supergene products were relatively near to the pre-Cretaceous surface surely had a significant role. Cook (1994) noted, "…*either copper enrichment or diagenesis of older supergene mineralization must have occurred after deposition of the base of the Glance conglomerate.*" This is a very real possibility.

To be clear, we believe that the vast majority, if not all, of the wonderful malachite pseudomorphs after azurite, found throughout Bisbee's mines, were formed during this first episode of supergene activity. An example is illustrated to the right. To support this position, the most substantial evidence for a single, district-wide event is the near-total absence of any azurite crystals of a centimeter or larger that are **not** second-generation azurite overgrowths on preexisting malachite pseudomorphs after azurite.

Two areas that did not experience this alteration were both protected by heavy coverings of supergene-derived, claylike manganese oxides. One is a very rich area on the 770 to the 900 levels of the Junction Mine that is of subaerial origin, and the other, much more limited in area, was on the 200 level of the Czar Mine, where only a part of an area was protected from alteration by Mn-rich clays. The Czar material, in contrast to the Junction mineralization, is of subaqueous origin.

Was subaerial azurite from the first supergene episode altered to malachite as well? We have not conclusively seen this in any of the hundreds of specimens studied, but it is difficult indeed to ascribe, with absolute certainty, early subaerial azurite and/or malachite deposition, except that from the 770 – 900 levels of the Junction Mine, which was not altered, as previously noted. There is no doubt, however, that the alteration of subaerial azurite to malachite was pervasive except in protected environments but unrecognized.

SECOND SUPERGENE EVENT:

The second supergene event occurred at some point during the mid-Cretaceous, after the Dividend Fault dropped the southern side a thousand meters or more, and the deposition of the Glance Conglomerate had begun. Cook (1994), using K-Ar dates of illite and alunite, dated a supergene event at 107-109 million years ago (ma). He did not recognize it as the second such event. He did, however, suggest the possibility that the alunite date was a reset. Our review of many specimens confirms this event and that it was largely, if not wholly, subaqueous.

This episode was far less intense than the first or either of the subsequent events. The most common feature of this event was the subaqueous deposition of second-generation azurite overgrowths on the earlier, pervasive malachite pseudomorphs in new layers of varying thickness or completeness. In several areas, manganese or iron oxides were deposited as paint-thin layers to little more than a brown/black stain before the new azurite deposition, thereby marking the event. Oft times, the new layer of azurite was later altered to malachite – blending so subtly with the previous malachite replacement of azurite that it can be detected only by very close examination. Few of the earlier pseudomorphs did not receive some degree of new epitaxial azurite deposition. In a few areas, mostly in the deeper levels of the Campbell Mine, subaqueous malachite, often zincian and not azurite, was deposited on the earlier malachite pseudomorphs after azurite.

Subaerial azurite and malachite from this episode have not been recognized, possibly masked by the later supergene events, which were dominantly subaerial and far more intense. However, the subaerial deposited copper carbonates in the Junction mine from the first event remained untouched due to the thick, massive manganese-rich clays/claylike materials maintaining an impermeable barrier. Other supergene minerals, particularly copper and cuprite, were again deposited during this second event in nonreactive environments of earlier supergene origin. Many Junction and Campbell copper specimens clearly demonstrate a second-generation partial overgrowth. These, too, were subaqueous in origin.

This second event was largely district-wide, although the southern-most area experienced little to no effect due to greater depth. The Paleozoic sedimentary beds were still relatively flat, thus pre-Laramide orogeny. The Cretaceous inland sea had advanced into southeastern Arizona by Albian time, covering what is now Bisbee (Hayes & Landis 1970). Further, Hayes and Landis (1970) show that ongoing burial by Cretaceous sediments was coincidental with the alunite dates of 107-109 Ma, Cook (1994).

This shallow inland sea, the “Bisbee-Mancos sea” of Scarborough (1989), had inundated the area over the relatively thin covering by the very porous Glance conglomerate and may well have initiated the second supergene event. Perhaps elements (Br, Cl, N) from the brackish, coastal waters entered the process. No doubt, the deepening sediments ended this relatively short-lived episode.

THIRD SUPERGENE EVENT:

This was followed by regional plutonism and tectonism of the Laramide orogeny in the Miocene. Uplift and some tilting accompanied by erosion occurred, which brought the mid to western parts of the district closer to the surface. The abundant NE-SW faults of the Copper Queen graben, which encompassed the mineralized zone, were variably reactivated. The third supergene episode took place after the mid and western areas were now closer to the surface and locally fractured and somewhat more eroded. This event was more intense due to the Paleocene paleoclimate, which was humid, temperate, if not sub-tropical (Nations et al., 1985).

It appears that most of the supergene activity in the mid-area was subaqueous, with both malachite and azurite deposited during oscillating periods. The uplift and tilting placed unoxidized sulfides physically up-dip above some of the existing supergene minerals and whose oxidation subjected earlier supergene minerals to alteration. Its general proximity to the Sacramento Stock, with higher pyrite content, presented lower pH environments that attacked the earlier carbonates while depositing copious amounts of supergene hematite with the copper carbonates. The now-inclined beds served as conduits for iron-rich, moderate pH solutions to migrate downward to the east, coating the earlier carbonates with goethite/hematite and forming abundant pulverulent hematite.

The western/southwestern parts experienced both subaqueous and subaerial activity, often fluctuating. Most of the copper carbonates were deposited as massive, in situ, or near-in situ replacement of the hosting limestones and as linings in boxwork forms.

The western-most area had substantial subaerial malachite deposited, often as in situ replacement of the hosting limestones. Malachite stalactites collected in the Czar and Shattuck mines by the authors were vertical oriented, indicated post-tilting deposition. Minor amounts of goethite were deposited as thin crusts or slight tinting on malachite. Goethite was abundant in pyrite-rich areas, as massive boxwork and even stalactitic forms, much of which was probably a replacement of earlier siderite due to continuous exposure to low pH solutions in a now oxygen-rich environment.

This cycle of weathering and enrichment was probably interrupted by the Basin and Range structural disturbance, which began around 17 million years ago in the early Miocene epoch. Additional tectonic activity and further tipping of the area by Basin and Range events may have caused the Copper Queen graben to have moved along the many northeast-trending faults, uplifting the remaining sulfides, exposing them to oxidation, and changing the solution pathways.

FOURTH SUPERGENE EVENT:

When the fourth and last supergene event began is uncertain. Cook (1994) gives a date of 9.08 Ma from alunite samples north of the Dividend fault, which seems reasonable, even though it is not possible to suggest what point in the cycle this date represents. In any event, this was an incredibly intense event. Indeed, it was the most intense of all, which was still ongoing in a minor way at the time of discovery in the late 1870s. A spring of bitter water was issuing from the base of Sacramento Hill, in testament to the active supergene alteration (Cox, 1938).

While mining, we passed through zones of varying, ongoing supergene activity as we moved east and down dip. In the west, the ores were largely completely oxidized, followed by a transition zone of mixed oxide and supergene sulfide ores and into largely fresh sulfides overlying by oxides to the east and finally to completely fresh sulfides at the eastern end and at depth. Pre-Cretaceous oxidation was found localized along the strong breaks, however.

Cook (1994) also indicates that there was no movement of the Dividend Fault between the last two events. This was based on the supergene blanket's continuity from the Cochise deposit to the Lavender Pit ores and beyond. Paleo-Pleistocene climate changes were frequent and often drastic, with extended periods of high precipitation (Nations and others, 1985). This enhanced the chemical weathering, which pushed many western supergene deposits to maturity.

Many of Bisbee's replacement deposits were totally and completely oxidized with last-stage oxidation products dominant, including the formation of oxidation caves. Moderate to low pH solutions altered the generally nonreactive schist and intrusives, mobilizing abundant aluminum forming clay and claylike deposits mixed with the iron oxides of hundreds of thousands of tons in volume. In one small area, the late aluminum-rich solutions attacked and replaced earlier copper and zinc carbonates and oxides.

And too, the large, wonderful malachite and azurite masses formed in a fluctuating combination of subaqueous and subaerial environments, most as in situ replacements of the hosting limestone, as oxidation reached full maturity. Azurite roses grew in abundance in the clays along a small portion of the hanging wall of the Dividend Fault very late in the process, while masses of cuprite and copper of many tons to tiny specks were formed in other nonreactive clay/claylike masses around the Sacramento Stock and in the adjacent limestones.

Cook (1994) has speculated on the duration of two episodes at Bisbee - 1.6 Ma for the Cretaceous cycle and 5.6 Ma for the Miocene-Pliocene phase. He did not recognize the two other episodes. The duration of the pre-Cretaceous and Laramide events is unknown. The latter phase, lumped together with late Paleocene to middle Eocene episodes, seems reasonable. As noted above, we believe the final episode continued through the Pleistocene and even into the Holocene epoch and present times, albeit at fluctuating levels as a function of the paleoclimates.

The contact between iron-rich clays and supergene altered limestone in the Holbrook Extension of the Lavender Pit Mine at an elevation of about 5,100 feet. Similar contacts can be seen in several places in the background. The lath with red flagging denotes ore-grade material (>5 percent copper) in the right side. The ore mineral was azurite in this case. A higher copper content was required to make grade as this material was direct shipping ore, as it could not be enhanced by milling, but sent directly to the smelter. The individual in this 1970 photo is Keith Coke, Chief Geologist. Graeme/Larkin collection.

Supergene alteration can proceed quitter rapidly. In the field, we have seen supergene-like activity progress very rapidly under the most ideal of circumstances—such as where mining had opened both oxidizing and fresh sulfide deposits to surface-like conditions. The oxidation caves, a prominent feature of the fully oxidized deposits in the western area, seem to have formed in the last several hundreds of thousands of years - nothing in geologic time -as geologically caves are ephemeral features, thus our hesitation in suggesting the duration of these supergene events, as no markers were left. Pliocene or later age, horizontally stratified goethite deposits are relatively common in the western area. These tell of a post-uplift age of formation.

A 20-meter-tall blasthole drill in the Holbrook Extension of the Lavender Pit Mine-1972. It was used to drill 30 cm dimeter, 17-meter-deep holes for blasting.

The pit walls show the varying effects of supergene alteration on differentially hydrothermally altered Escabrosa limestone areas.

The upper-left quadrant is largely badly broken, recrystalline limestone with iron oxide staining along some boulder faces. Subsidence caused by supergene alteration broke up this thick bedded rock unit.

Moving downward, the soft, reddish -colored hematite clays hosted an orebody as shown by the remaining support timber visible at its bottom and on top of the yellowish/brown clays.

The soft yellow clays were derived from intense, supergene action on hypogene altered limestone. The marks left by the teeth of a large electric shovel bucket show the soft nature of the material. Graeme/Larkin collection.

Less certain is the number of supergene episodes affecting the Sacramento Stock Complex as the mineralogy varied little over the successive events. Different sections of the Complex reflect probable differing paleosurface topography. And too, the supergene minerals in the Sacrament Stock Complex were far more susceptive to remobilization and redeposition in this nonreactive environment, without leaving a trace of the event(s). However, inasmuch as the Sacrament Stock Complex is in the mid to west part of the mineralized area, and a relative topographic high, cut by the Dividend Fault, it may have experienced more or extended episodes of supergene activity.

In the limestone hosted mineralization, only the first two episodes were near district-wide, the third impacted the mid to western part of the mineralized area, while the last episode of supergene alteration only took place in the western and southwestern parts. The recognized events seem to be related to cycles of landscape development. The combination of uplift, "mountain growth," and lowering of base levels produced physiographic conditions most favorable for enrichment; as Cook (1994) reports, based on work by Atwood (1916), Evidence for this correlation was found at other similar porphyry deposits in the Southwest.

SUPERGENE MINERALS

There is little doubt that some of the supergene species from Bisbee are among the finest of their kind in the world. The unparalleled variety in form and color in which several of the more important species occur is unmatched. This, along with a wide range of secondary species, has further has added to the fame of Bisbee as a producer of exceptionally fine and rare minerals. Below is a list of those species recognized as having formed under supergene conditions. Some of the below-listed species have other, often more frequent, modes of occurrence but are included here for completeness.

The wide variety of minerals that formed under supergene conditions at Bisbee reflects an expansive range of depositional environments, often isolated, with variable hypogene mineralogy, differing supergene solution chemistries, as well as multiple supergene events. In many instances, the minerals from an earlier supergene environment changed over time with burial by post-ore sediments and later tilting and/or uplift coupled with other supergene episodes. The earlier formed supergene minerals in some areas were exposed to low pH solutions of variable chemistry following tilting, which lifted fresh or oxidizing sulfides up-dip, forming a different suite of species, often at the expense of the earlier supergene minerals.

allophane
alunogen
alunite
anglesite
antlerite
aragonite
atacamite
aurichalcite
austinite
azurite
barite
bandylite
bayldonite
bayleyite
beaverite-Cu
beudantite
bindheimite?
bisbeeite
bismite
bismutite
böhmite
bornite
botallackite
botryogen
braunite
"braunite II"
brochantite
bromargyrite
buttgenbachite
calcite
caledonite
carbonate-cyanotrichite
cerussite
cesárolite
chalcanthite
chalcoalumite
chalcocite
chalcophanite
chalcophyllite
chalcopyrite
chalcosiderite
chlorargyrite
chrysocolla
claringbullite
clinoatacamite
clinoclase
conichalcite
connellite
copper
copiapite
coquimbite
coronadite
covellite
crednerite
cryptomelane
cuprite
cuprotungstite
cyanotrichite
delafossite
descloizite
devilline
diaboleite
digenite
dioptase
djurleite
dolomite
duftite
eddavidite
endellite
eugenite
felsőbányaite
ferrimolybdite
fornacite
furutobeite
galena
gerhardite
gibbsite
goethite
gold
goslarite
graemite
graphite
groutite
gypsum
halloysite-10Å
hausmannite
hematite
hemimorphite
hetaerolite
hisingerite
hoganite¿?
hydrobasaluminite
hydrocerussite
hydrohetaerolite
hydrozincite
iodargyrite
johannite
jarosite
kaolinite
kettnerite
ktenasite
langite
leadhillite
lepidocrocite
likasite
linarite
liroconite
malachite
melanterite
manganite
massicot
miersite
mimetite
minium
mottramite
murdochite
nambite
nantokite
neltnerite
nolanite
nordstrandite
opal
osarizawaite
paramelaconite
paratacamite
paracoquimbite
paratellurite
pharmacosiderite
phosgenite
planchéite
plattnerite
plumbojarosite
powellite
pseudomalachite
pyrite
pyrolusite
pyromorphite
quartz
ramsdellite
ransomite
ralstonite
rhomboclase
romanèchite
römerite
rosasite
scorzalite
sengierite
sepiolite
shattuckite
siderite
silver
smithsonite
spangolite
spertiniite
sphalerite
spionkopite
stibiconite?
stolzite
stromeyerite
sulfur
tangeite
teineite
tellurite
tenorite
tilasite
tolbachite
torbernite
turquoise
tyrolite
tyuyamunite
uranopilite
vanadinite
variscite
volborthite
voltaite
willemite
wulfenite
zippeite

Table 8: List of the secondary mineral species recognized at Bisbee, Arizona

Those noted in *italics* indicate that the species is no longer considered valid, while a? indicates a questionable status as a valid species, while ¿? is used where the species occurrence may be manmade. These are included to allow for referencing the historical identification in earlier studies by those who have studied Bisbee in the past.

SUPERGENE OREBODIES:

To better understand the occurrence of the desirable supergene minerals at Bisbee, a bit of information on the orebodies is helpful, as is the understanding that the specimens recovered were but a very minor, if not a minuscule part of the secondary orebodies. This is not to say that many of Bisbee's treasures were treated as mere ore. Indeed, the vast majority of good specimens were always appreciated and recovered; they were just never common.

As noted under mineralization, the hypogene deposits were an agglomeration of copper/iron/lead/zinc/sulfur with minor accessory metals and metalloids in a wide variety of mineral species. The copper deposits were encased in or peripheral to relatively huge replacement masses of pyrite. This characteristic was clearly manifested in oxidized/oxidizing deposits.

Minable ore was more a function of economics than mineralogy. It cost considerably more to mine, move, smelt, etc., soft, unstable oxide deposits than other ore types; thus, a higher grade was needed to make these soft ores economic. Smaller, isolated, or distant deposits were often not mined because of the development and operating costs associated with their exploitation.

In the most general of terms, three broad types of supergene deposits will be touched upon, reflecting the differences brought by varying degrees of supergene alteration. Only the limestone replacement deposits are considered, as the porphyry-style deposits at Bisbee are well documented by numerous other workers and rarely contained anything of collector interest. Those to be discussed are:

> MATURE; fully oxidized deposits were those from which virtually all of the sulfur has been removed, and a good deal of the iron has been mobilized, if not transported, and the copper minerals are in general equilibrium with surface/near-surface conditions. These were warm (+80^{0}F - 27^{0}C), usually wet, humid environments, with many below the water table, as it existed at the time of discovery. To be sure, few deposits were truly fully oxidized, with just malachite and chrysocolla remaining as the copper minerals. The original Copper Queen orebody, which contained very little azurite and even less cuprite, was one of the few. However, most of the orebodies mined early on were well on the way to supergene maturity.
>
> ADVANCED; oxidized where little, if any, pyrite remains, and the few copper sulfides that remain are mostly supergene in origin with the great majority of copper as carbonates, oxides, the element, insoluble sulfates, or modest amounts of supergene sulfides. These were warm to hot areas (+90^{0}F - +32^{0}C), humid, below the existing water table, but the stage/depth of oxidation is not related to the present water table.

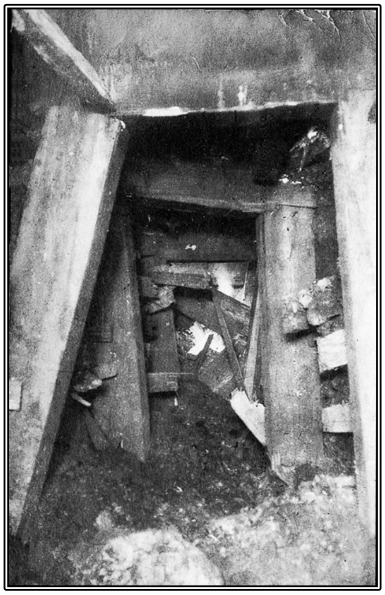
INTERMEDIATE; Those deposits where oxidation is still aggressively underway, with much of the pyrite oxidized and the copper is largely mobilized and forming secondary copper sulfides, except at the limestone interface where carbonates are forming. Elemental copper is forming in nonreactive clays and rocks. Sulfide oxidation is an exothermal process. Thus, these are hot to very hot environments (+100^{0}F - +38^{0}C) relatively dry with a CO_2-dominant atmosphere until opened and ventilated.

MATURE OXIDE DEPOSITS:

This is the type of deposit that was mined during the early years of exploitation, those which were near-surface and had experienced more intense multi-supergene alteration events. They were restricted to the western portion of the district. Except for the original Copper Queen orebody, which was three meters from the surface, supergene activity was not totally complete for most deposits; indeed, it was ongoing at the time of discovery. Continued, it would ultimately convert all the copper minerals to malachite and/or chrysocolla, but effectively, all sulfur had been removed and iron converted to oxides with much transported, creating often substantial open spaces above.

Much of the iron oxides were relics of the barren pyrite, which contained little to no copper. The iron oxides were intimately mixed with supergene-derived clays and claylike minerals from the altered limestones, creating a worthless, challenging material, which had to be mined in the endless search for ore.

Locally referred to as “ledge matter,” it held the orebodies within or at the periphery, reflecting the original locations of the high pyrite hypogene carbonate replacement deposits. Most of what was mined was used for backfill in mined-out areas. Generally, the ledge matter was very soft and plastic, some even near fluidlike, and complicated to support for mining, adding cost; thus, requiring a higher copper content of the ores to be economical.



Right: A heavily timbered crosscut, squeezed closed by the unyielding pressure of the plastic clays. The vertical and top timbers were 30 cm square. Holbrook Mine, circa 1904. Graeme-Larkin. collection

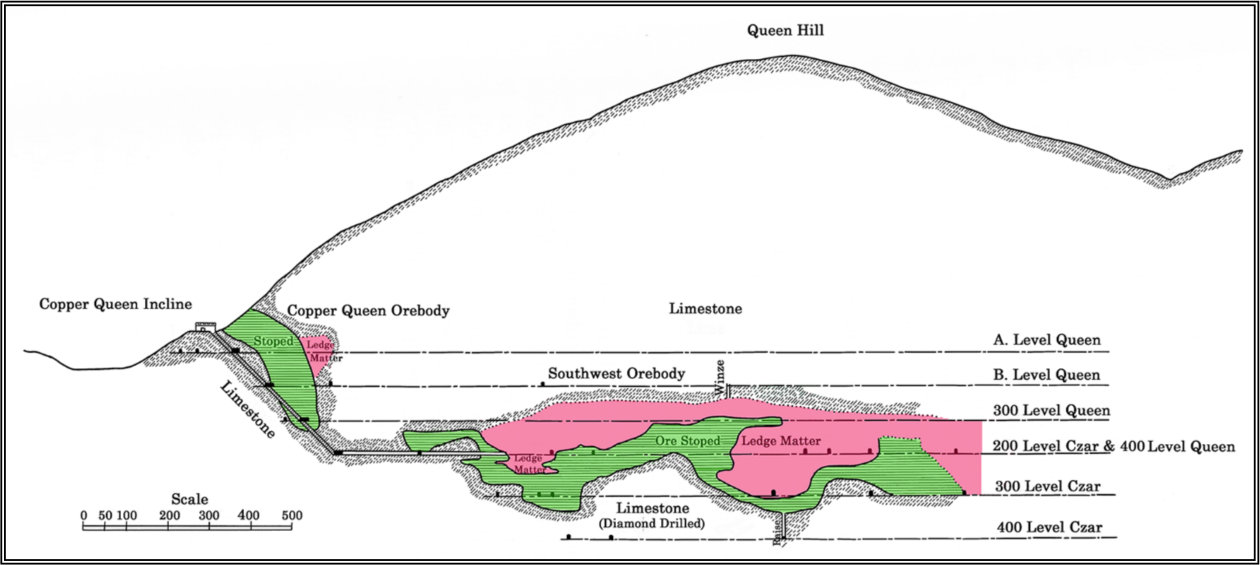
As illustrated above, just keeping the access open was a constant challenge, with 30 board feet of timber used for every ton of heavily oxidized ore mined. Even then, an opening could close in a day’s time. Fortunately, these clays could be mined with just a pick. If blasting was required, an auger was used to drill short holes. Douglas (1900) estimated that in excess of 10,000,000 tons of ledge matter had been found at the time of his paper.

Further, Douglas (1900) wrote that it was common to drift for hundreds of feet through these barren, iron-rich clays with no indication of ore, then suddenly find them carrying good copper grades, but visually indistinguishably from the low/non-copper clays. The assay test of every face, every day was essential. The copper occurred as minute specks and flakes of cuprite, black oxides, and/or elemental (native) copper. If the ore mineral was malachite, it was obviously ore of good grade with the malachite as streaks or scattered nest of acicular crystals (Douglas, 1900).

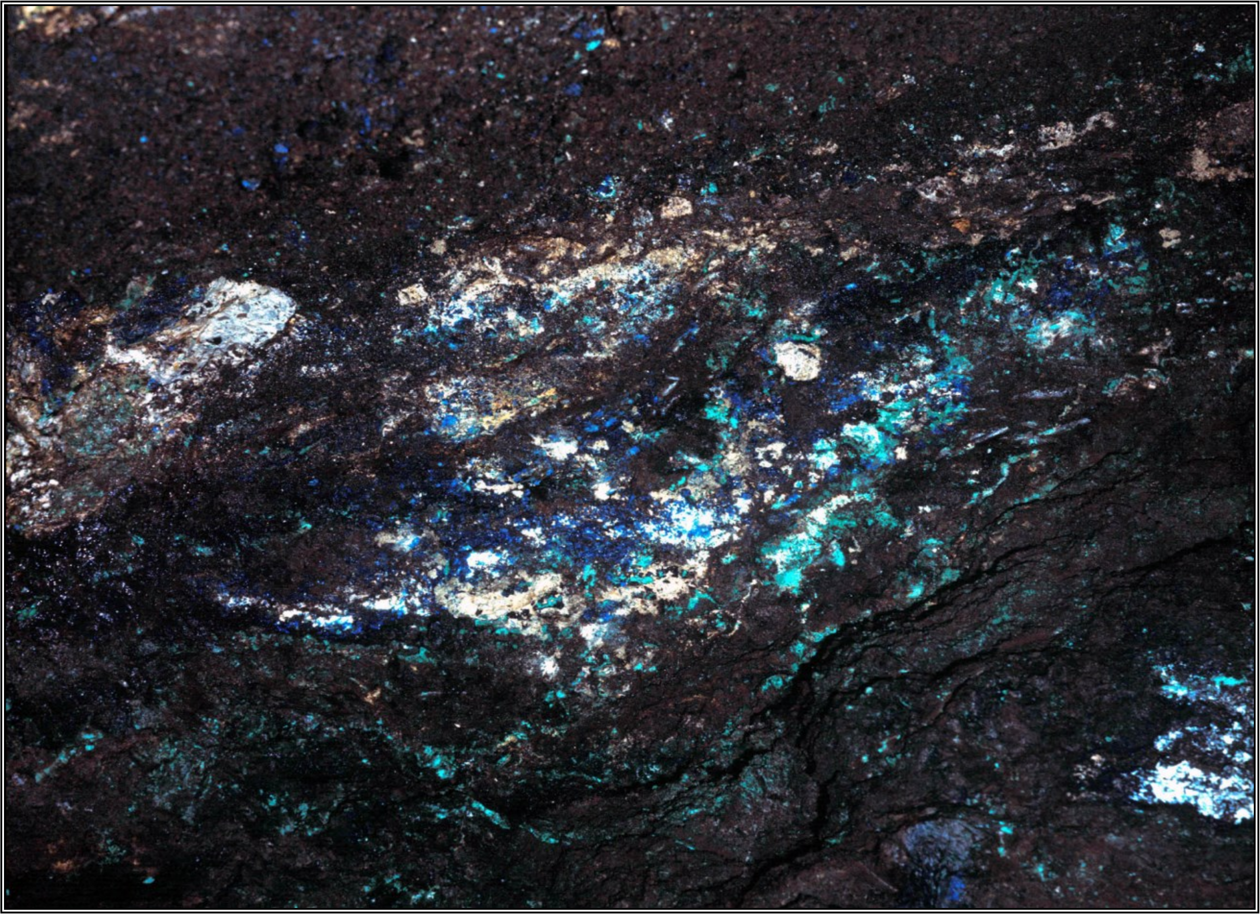
From a specimen production standpoint, these were the best deposits, starting with the Southwest orebody in 1885, though mining was suspended for a while due to low copper prices. By late 1887 mining resumed (Douglas, 1900), and azurite crystals, as never seen before (English, 1890) occurred in the boxwork goethite along the edges of the orebodies, while large plates and sizable vugs of botryoidal azurite and malachite were found in abundance at the limestone interface, which were collected and preserved.

A fully mature, malachite/goethite/hematite supergene orebody with abundant boxwork voids and calcite, which was so common, 5th level, Southwest Mine, view-2.8 meters, grade ≈ 5 percent copper Graeme/Larkin collection.

The clay masses were usually huge, with a relatively small portion reaching ore grade (>7% Cu). Often this grade was achieved only by rough hand-sorting in the stope, leaving waste behind for the essential backfill (Douglas, 1900). The claylike ore that was not close to the limestone host rock or well mineralized was usually visually challenging to distinguish from the waste. This complicated hand sorting; removing waste rock for use as backfill, which was a standard procedure to maintain a high grade. It was more economical to remove the waste from the ore underground than to have it trammed, hoisted to the surface, and smelter. This process lasted until about 1915, when increasing labor costs made it less economical.

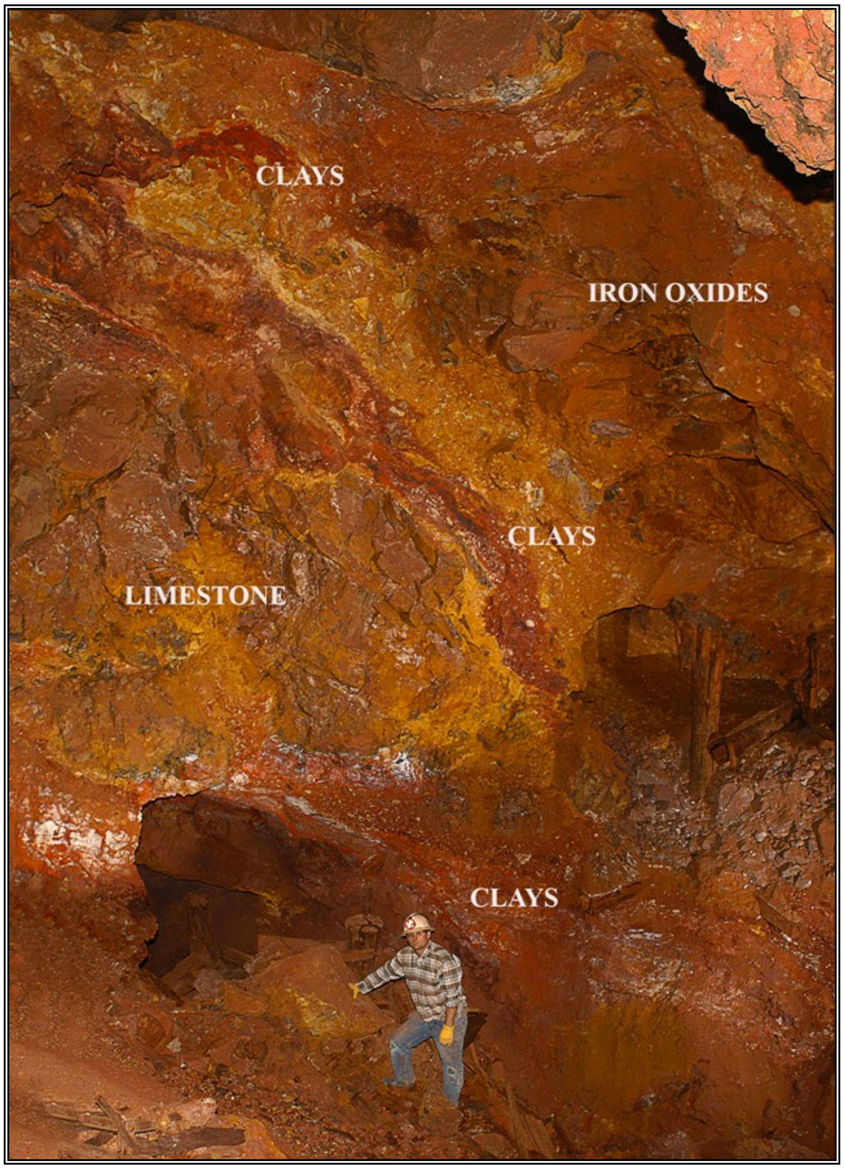


The Southwest orebody, figured above, produced many of Bisbee's very best crystallin azurite specimens, as well as fine botryoidal malachite and azurite masses. Most came from the ore-limestone interface areas. Fine cuprite and copper specimens came from claylike ores just below the "ledge matter." After Douglas, 1900.



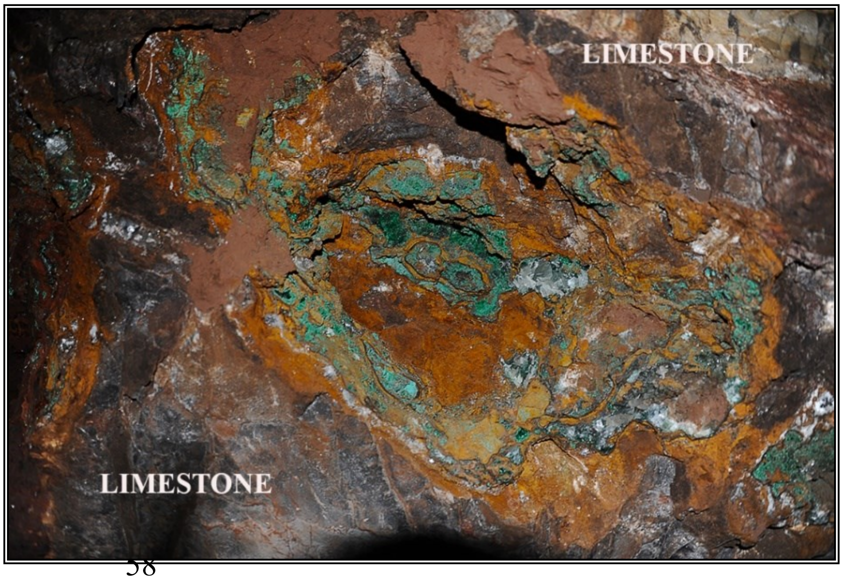
A fully oxidized orebody of malachite and azurite with manganese oxides in altered Martin limestone, 770 level, Junction Mine, view-2.4 meters. Grade ≈ 7 percent copper. Graeme/Larkin collection.

Many of the oxide orebodies were in somewhat more competent rock, but substantial support timber was still required, and frequent, tight backfilling of the mined-out areas essential. Mining was safer and cheaper, where the rock was more competent. A copper content as low as 5% was economic, with copper carbonates the typical ore minerals. These were often specimen-rich deposits, particularly near the limestone contact.



Right: oxide shell surrounding a mined-out, fully oxidized orebody.
The compressed mix of hard iron oxides, iron-stained clays/claylike materials and residual limestone was typical of the non-ore grade shells around fully oxidized orebodies.
Also, a large, well decorated oxidation cave was found some 20 meters above this area. 12 stope, 7th level Southwest Mine. Graeme/Larkin collection.

Also, adjacent to the hosting limestone, goethite developed as masses with boxwork, botryoidal and stalactitic forms, often as replacement of siderite. This goethite frequently served as a base for the deposition of low pH minerals such as copper and near-neutral species such as azurite, malachite, and quite often, calcite.



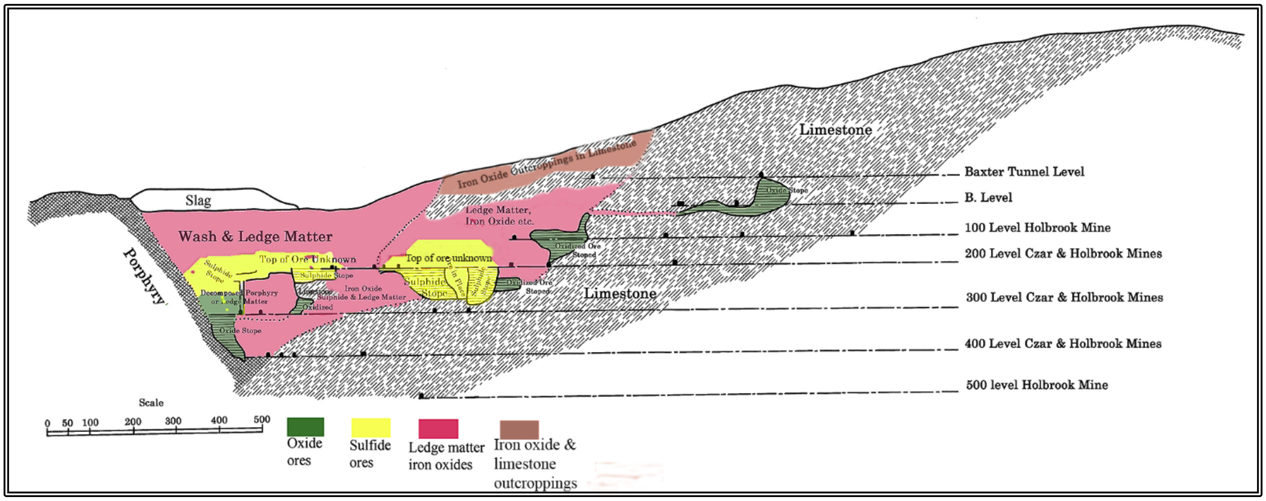
Right: Malachite lining goethite boxwork voids with minor calcite. This formed at the margin of a very large, fully oxidized orebody with unaltered limestone. View-2 meters, 14 stope, 5th level Southwest Mine. Graeme/Larkin collection.

ADVANCED OXIDIZED DEPOSITS:

Disseminated supergene chalcocite, as replacements of pyrite in deeply altered limestone, altering to brochantite along a fault. View-1.2 meters, 5 stope, 6th level Southwest mine. Graeme/Larkin collection.

As mining followed the orebodies to the east and greater depths, the new orebodies were less oxidized. Some sulfides remained, including modest amounts of disintegrating pyrite, with copper mostly as supergene minerals. Species from the chalcocite group, which were deeply oxidized as well, were the more common. The increasing depth, coupled with less intense and fewer supergene episodes, had yet to complete the total chemical weathering.

Supergene alteration obviously begins along the various interfaces of the replacement deposits with the host rock, following breaks and structural features through which oxidizing agents might enter. The nature of the host rock and hydrothermal alteration effects could and did play an essential role in the entry and circulation of groundwater as well as supergene fluids.



The various oxide and sulfide ores noted in the above illustration were parts of a single large orebody that, while deeply oxidized, still contained substantial supergene sulfides such as chalcocite group minerals and covellite. The section is looking southeast. After Douglas, 1900.

The whole of the Sacramento Stock Complex is surrounded by rocks, which were hydrothermally altered to varying degrees, as well as massive supergene-derived clays/clay-like minerals, notably along the western and southern sides. These soft, largely low-permeability materials greatly impeded chemical weathering of the encased sulfides. This is demonstrated in the illustration above, where completed oxidation is largely restricted to the parts of the deposits not entirely surrounded by clays. Notably, the remaining sulfides were almost totally supergene replacements of hypogene sulfides. An exception was the rich ores in the intrusion breccia, which was largely rendered mostly impermeable by intense silicification.

Left: A 22 cm mass of hypogene chalcocite altering to coarsely crystalline malachite. Minor calcite is present. 1500 level, Junction Mine, Graeme collection

Along the limestone interface, it was common to find the copper carbonates developed just as was seen in more mature deposits. Boxwork malachite and azurite forms were abundant at this interface and into the hosting carbonates for a meter or more. Goethite boxwork forms were also abundant, often within huge masses of pyrite-derived goethite. These voids hosted malachite and/or azurite, calcite, copper, cuprite, as well as combinations of these species, reflecting evolving environments.

Within the orebodies, the difference of the stage of alteration was apparent, as supergene alteration begins at the edges and along faults and other structural features. Incomplete alteration of the minerals was common with the residual or newly deposited supergene sulfides more or less surrounded by minerals, which were more advanced in the chemical weathering phases. Chalcocite group minerals in varying stages of

Supergene chalcocite altering to cuprite and copper with goethite. Minor calcite is present as veins. View-8 cm, Cole Mine, Graeme collection

replacement by malachite and/or brochantite were abundant in high-grade areas. Less common was the in-situ replacement of both supergene and hypogene chalcocite to cuprite and/or copper.

Both Douglas (1900) and Ransome (1904a) studied this closely, and both reported that it was common to find the supergene chalcocite altering into copper and cuprite in several locations where it was associated with pyrite and/or iron oxides. Alteration directly to malachite was also noted by both workers, which was commonly seen over the years when limestone was present.

Supergene copper minerals were far more diverse in this environment. They ranged from carbonates in reactive rocks; to hydroxyl sulfates to soluble hydrated sulfates and with copper as well as cuprite along with supergene sulfides in the clays and non-reactive rocks. Iron was most commonly found as minor, residual oxidizing pyrite, siderite, and abundant goethite in huge masses, with stalactitic forms common. Solutions generated by later oxidizing copper sulfides, particularly chalcopyrite, often deposited azurite and/or malachite as crystals on goethite boxwork in subaqueous environments or coatings in subaerial settings. Evidence of fluctuating subaqueous/subaerial environments was seen in many specimens.

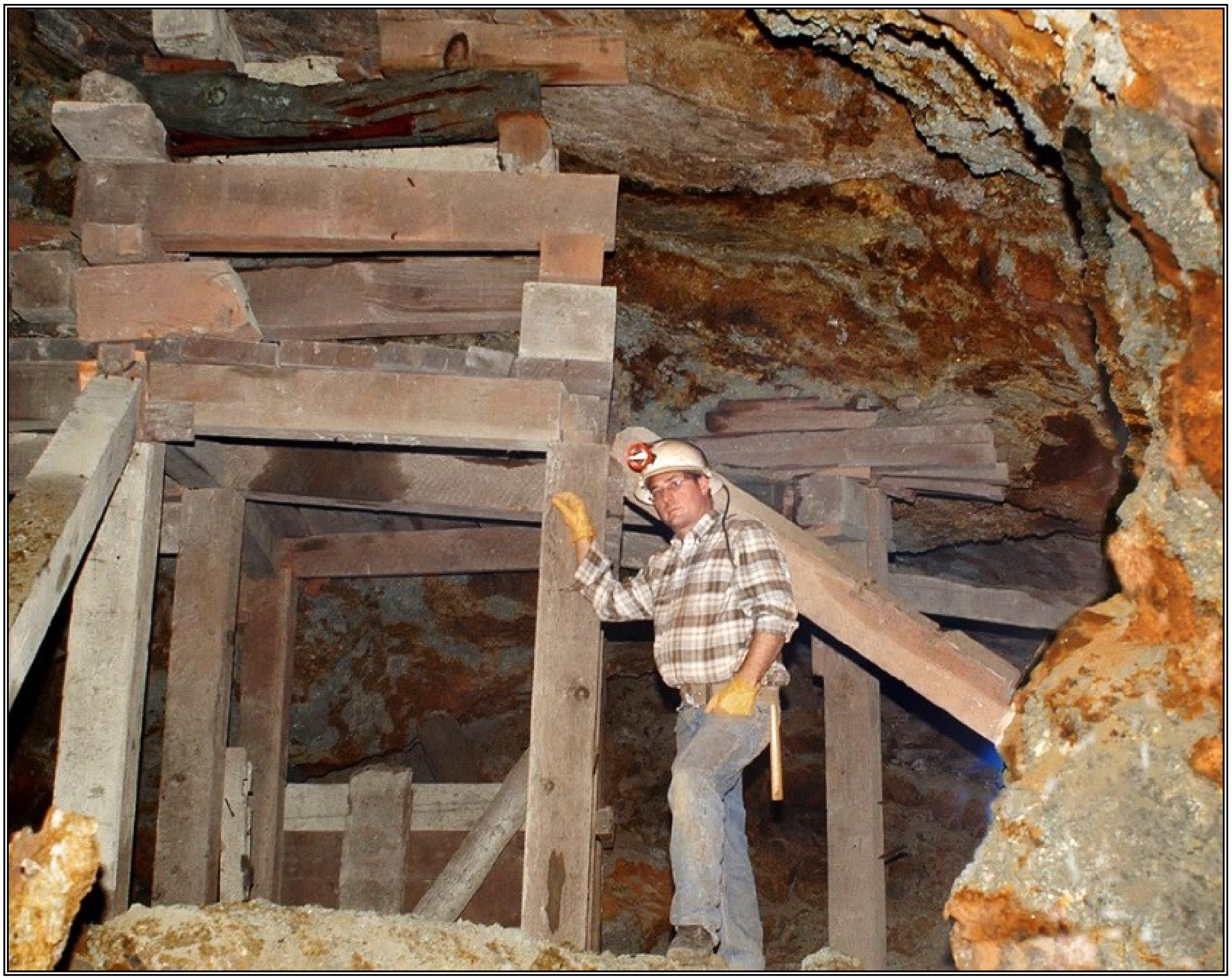
In as much as sulfur was still present, often abundant, and a good deal of iron had not yet been transported, open spaces did not develop over the oxidizing ores, as seen over mature oxide deposits. Further, the otherwise pervasive alteration clays/claylike/iron oxide mix was far less developed; thus, some rock strength remained, making mining more manageable and safer.

Intermediate Oxidation:

The supergene minerals in this environment found depended on the encasing rocks or the proximity of limestone. When within pyrite, chalcocite was abundant as coatings, often soot-like and/or as a replacement of pyrite. Assay tests often indicated the pyrite to be low in copper content, but when supergene chalcocite was present, the copper grade increased dramatically, even making ore grade.

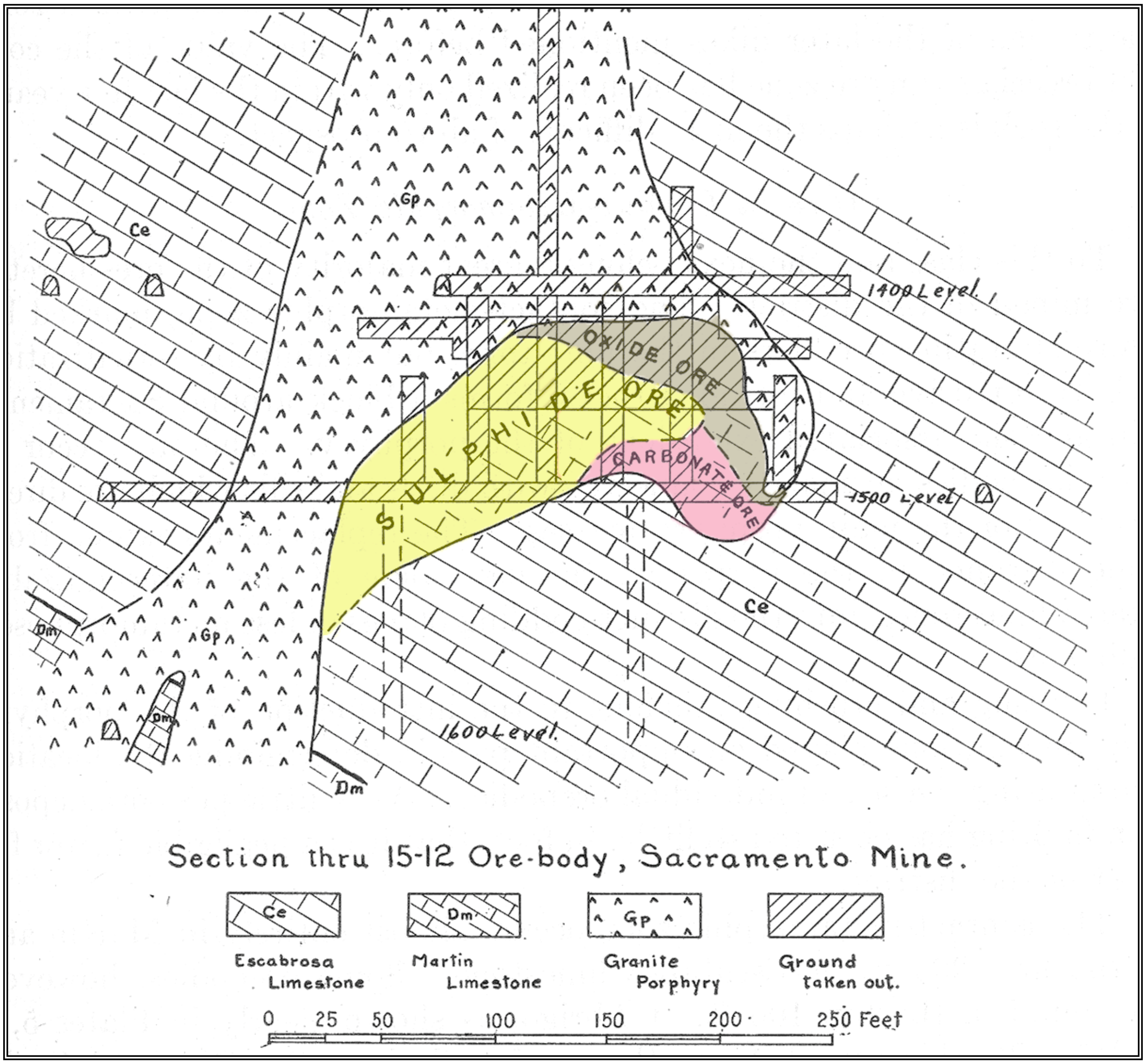
Right: Black, sooty, supergene chalcocite on pyrite, specimen-7 cm, Gardner Mine, Graeme collection.

A goethite rind surrounding oxidizing pyrite, specimen-5 cm, Gardner mine, Harvard Museum specimen. Graeme/Larkin collection.



Oxidizing, low-grade pyrite shell that encased a sulfide orebody. Note the mine timber condition - almost like new - yet it had been installed more than 70 years before. The very dry, typically warm environment that is found with oxidizing pyrite has preserved the wood. One of the authors, RWG IV. is in the photo.7th level, Southwest Mine. Graeme/Larkin collection.

In the below illustration, from Bonillas et al. (1916), an ore grade, primary sulfide mass deposited in an embayment of a porphyry a dike is undergoing oxidation. Where the encasing rock is nonreactive, such as sulfides or porphyry, the supergene products are oxide ores, a term used to indicate elemental copper and/or cuprite. When limestone is the encasing rock, carbonate ores formed.



Section through an oxidizing orebody on the1500 level, Sacramento Mine, showing the influence of the host rock on the supergene alteration products, after Bonillas et al. (1916).

DEVELOPMENT OF SUPERGENE MINERALS

The time needed to bring an oxidizing deposit to full maturity - the complete removal of sulfur and transport of the mobile metals - is dependent on several conditions. The most important of these is the availability of oxidizing agents. These include groundwater (chemical weathering), exposure to near-surface conditions due to uplift and the resultant erosion (mechanical weathering) reducing cover. Also, faulting/fracturing, which creates pathways for fluid movement, is important. As noted previously, the mineralized areas at Bisbee were variously subjected to changing conditions over their more-or-less 200 million years of existence.

Due to depth or a protective cover, most of the individual replacement deposits were not fully oxidized. Indeed, many, if not most, were never ever subjected to the conditions which cause supergene alteration, particularly in the eastern and parts of the mid areas. The easternmost deposits were deeper, whereas uplift and tilting brought the western areas closer to the surface into an environment favorable to supergene alteration.

A brief review of several of the more important depositional environments at Bisbee follows. To better understand how the minerals formed and why one species was preferentially deposited in a given environment, a quick look at the chemistry is helpful. This is a most general overview and, therefore, less than complete, notable by not discussing the thermodynamics of the redox regime. With this caveat noted, carbonate is critical. Douglas (1900) noted that the copper carbonates at Bisbee always occurred in close proximity to the hosting limestones. This is why.

Carbonate availability was a prime driver in the formation of supergene minerals at Bisbee. The host carbonate rocks reacted with the acidic, supergene solutions causing carbon dioxide (CO_2) gas (g) to be generated in huge quantities, with the gas phase in the supergene zone (perhaps locally) becoming essentially 100% CO_2(g). This had a profound effect on the development of the supergene mineral assemblage. It was the amount of CO_2 present that drove the preferential formation of azurite or malachite. A subtle interplay of chemical and physical factors is involved, but the preferential formation of malachite and/or azurite at higher pressures of CO_2 (adjacent to a carbonate source, i.e., limestone) is easily rationalized through the above considerations. The process may operate on both macro and micro scales.

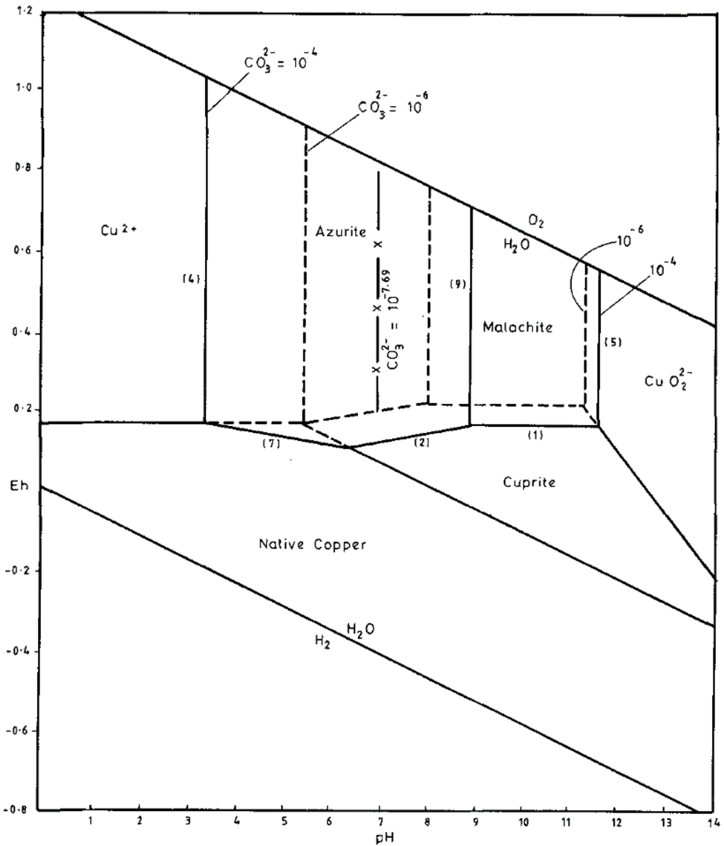
Now the possibility arises to have malachite or azurite deposition depending only upon the partial pressure of CO_2(g). For the following equation at 298.2 K, with the partial equilibrium pressure (p) of CO_2 is $10^{-1.36}$. Note that atmospheric p(CO_2) is $10^{-3.5}$ (Williams, 1990).

$$3Cu_2CO_3(OH)_2\ ((s)\ \text{malachite}) + CO_2(g) \leftrightarrow 2Cu_3(CO_3)_2(OH)_2\ ((s)\ \text{azurite}) + H_2O(l)$$

If p(CO_2) is $10^{-1.36}$, both minerals crystallize at equilibrium; if p(CO_2) $<10^{-1.36}$, malachite forms; if p(CO_2) $>10^{-1.36}$, azurite crystallizes. Fluctuations of p(CO_2) will give rise to replacements, and multiply banded copper carbonates will form if not all of the pre-existing material is reacted away under changing solution conditions. The new material crystallizing on the surface simply protects what is present and underneath (Peter Williams, personal communication, 2010).

There are environments where azurite – azurite/malachite – malachite are all stable, and the earlier deposited material is unaffected by, the later identical solutions. Malachite has a broader range of stability, thus, rarely shows the corrosive effects of later, lower pH formed azurite, which seems to have been uncommon at Bisbee, excepting the azurite roses along the Dividend fault. The below Eh-pH diagram from Vink (1986) illustrates this. However, azurite is sensitive to pCO_2 and alters readily to malachite, as referenced above.

Concerning azurite and malachite formation, Vink (1986) wrote: *"It is shown that stability relations of these minerals can be better explained in terms of activities of the carbonate and bicarbonate. Azurite can be formed only under relatively acid conditions at relatively high carbonate activities. Since the latter imply mostly basic conditions, this explains why malachite is the more common form of copper carbonate and that azurite can be formed only under rather unusual conditions. It also explains the frequent alteration of azurite into malachite, due to small changes in carbonate/bicarbonate activities. These alterations include pseudomorphs of malachite after azurite."*



Partial Eh-pH diagram of the system Cu-O-H CO 2 at 25 ~ and 1 atm. total pressure. Total dissolved copper ion: 10 -6 molal. The diagram shows the stability fields of malachite and azurite as a function of pCO_2. Equilibrium is reached at $pCO_2 = 10^{-3.45}$, atm. with corresponding pH = 6.95, pH = 13.05 and Eh = + 0.670-0.0592 pH (straight lines). (after Vink, 1986)

As noted, oxidizing primary sulfide minerals often directly formed carbonates such as azurite, malachite, and siderite when in direct contact with limestone. With continued supergene activity, these too would ultimately alter to malachite or goethite. This is due to the reduced generation of CO_2(g) as a result of reduced acidic solutions reacting with limestone.

It is now appropriate to turn to the question of malachite or azurite formation versus cuprite, in line with the carbonates forming preferentially when the setting is close to the limestone contact. For this purpose, the following equation involving malachite is essential.

$$Cu_2CO_3(OH)_2\ ((s)\ malachite) + 2H^+(aq) + 2e^- = Cu_2O((s)\ cuprite) + CO_2(g) + 2H_2O(l)$$

Malachite is reduced to cuprite at a given pH, which is simply dependent upon the partial pressure of CO_2 and Eh. The increase of the latter will serve to lower the potential at which cuprite is the stable phase. In other words, at a constant potential, there are elevated pressures of CO_2 that will cause malachite/azurite to form and lower pressures of CO_2 that will lead to the crystallization of cuprite. A subtle interplay of chemical and physical factors is involved, but the preferential formation of malachite at higher pressures of CO_2 (adjacent to a carbonate source, i.e., limestone) and cuprite further away from available carbonate is easily rationalized through the above considerations. The process may operate on both macro and micro scales, and similar equations could be generated for azurite versus cuprite if $p(CO_2) > 10^{-1.36}$, as set out earlier.

Only when CO_2 was either not available or present, even in small amounts, do other common supergene species such as chalcocite, covellite, copper, and brochantite form. This invariably occurs in nonreactive environments that are often physically isolated and impermeable, precluding changes in atmospheric/solution gas composition or dissolved content. Once the nature of the surrounding gas changes, be it atmospheric or dissolved, alteration of the earlier species often begins. Malachite and/or chrysocolla with goethite are the end products of continuing supergene alteration. Information on this process is available in Smith and Martell (1976), Williams (1990), Robie and Hemingway (1995).

SUPERGENE MINERAL DEPOSITIONAL ENVIRONMENTS:

The following is a brief discussion of some of the more important or unusual environments that have produced some of Bisbee's most notable minerals. This is not intended to discuss the supergene processes in general, but rather a very brief overview to give a better understanding of the genesis of the depositional environments discussed and how their characteristics governed what minerals were deposited and preserved.

The hypogene minerals, as deposited, usually occurred in diverse mixtures but were generally dominated by one or more ore-mineral assemblages as described by Schumer (2017). Pyrite was always the dominant sulfide present, and it was pyrite oxidation that drove and governed the overall individual orebody supergene alteration.

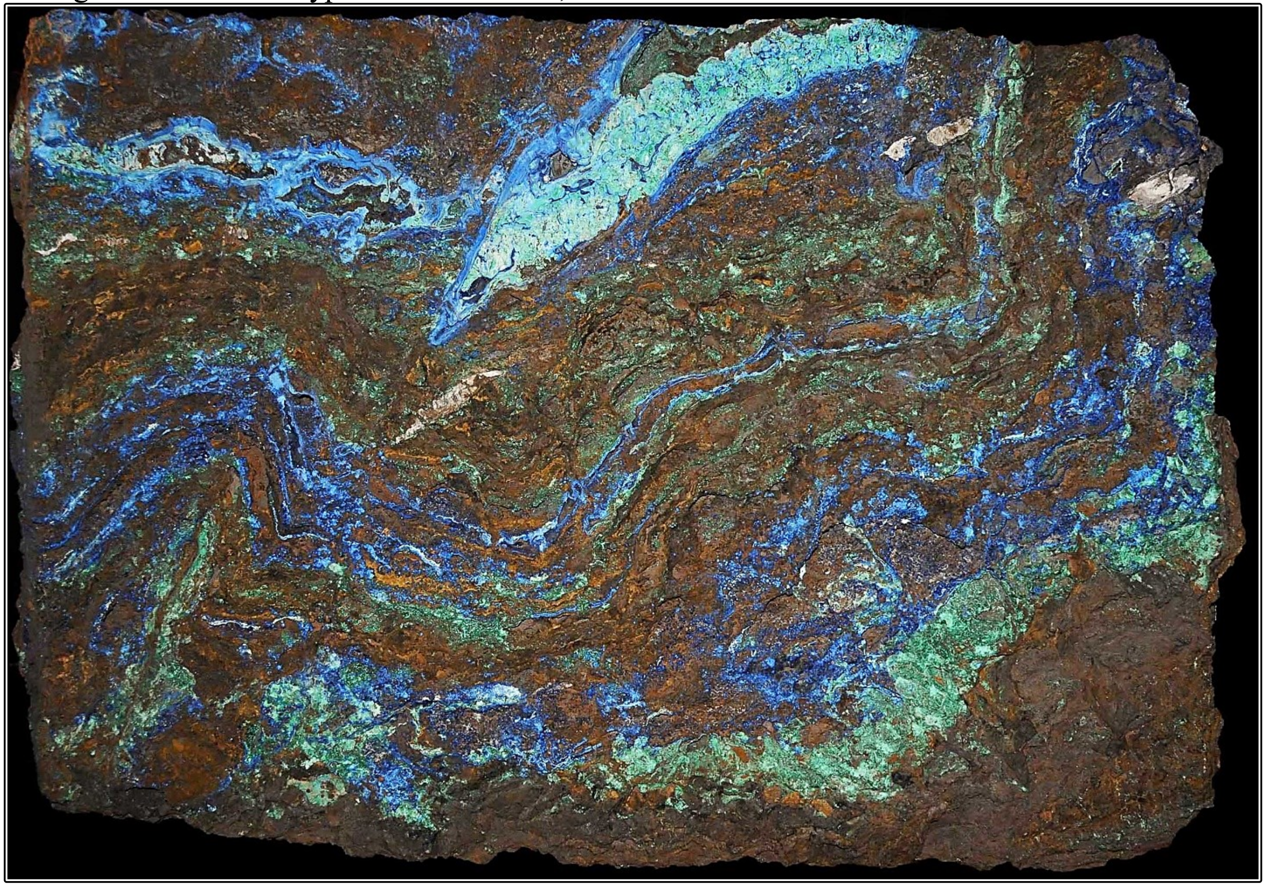
In a supergene environment such as found at Bisbee, pyrite was the first sulfide mineral to oxidize, generating an acidic environment dominated by mobile solutions high in Fe^{2+}, which with continued oxidation led to Fe^{3+} solutions. These acidic solutions attack both the encasing limestone, generating CO_2, and the other metal sulfides, liberating copper and/or other contained metals. Abundant pyrite generates large volumes of low pH solutions, which migrate through the encasing limestone, forming siderite. Continued exposure to low pH solutions ultimately alter the siderite to goethite and the noncarbonate rocks to clays and clay-like minerals, as CO_2 is reduced and O_2 increases.

The removal of the sulfur from pyrite and other sulfides by oxidation creates voids, as does the removal of iron and the other metals mobilized represents a complete breakdown of the minerals. The metals are redeposited elsewhere, as any number of minerals, depending on the chemical, physical and atmospheric conditions where equilibrium is reached. Remobilization and or alteration often occurs as renewed oxidation occurs, resulting from mechanical weathering, bringing near-surface conditions. Other events that played a minor role, such as tectonic movement or uplift and the opening or disruption of solution channels, have a direct impact on mineral deposition. Several environments are discussed below: 1). in-situ deposition, 2). development of boxwork forms, 3). soft, non-reactive, claylike depositional environments, 4).

massive cuprite nodules, and 5). oxidation caves. While several of these environments often combined to make up the oxidation cave occurrences, these caves are important enough to discuss independently.

In Situ Deposition:

As discussed previously, the hypogene sulfide minerals were deposited as replacements of the host limestone. These replacements were most often quite faithful in preserving the limestone's features, such as bedding, structure, chert beds, etc. Even fossils were often preserved. In situ supergene deposits frequently retained many of these primary sedimentary features. Typically, these relic features were relatively small when compared to the whole of the deposit. However, inasmuch as some of the finest examples of large, massive, botryoidal malachite and azurite have their geneses with this type of environment, a discussion is warranted.

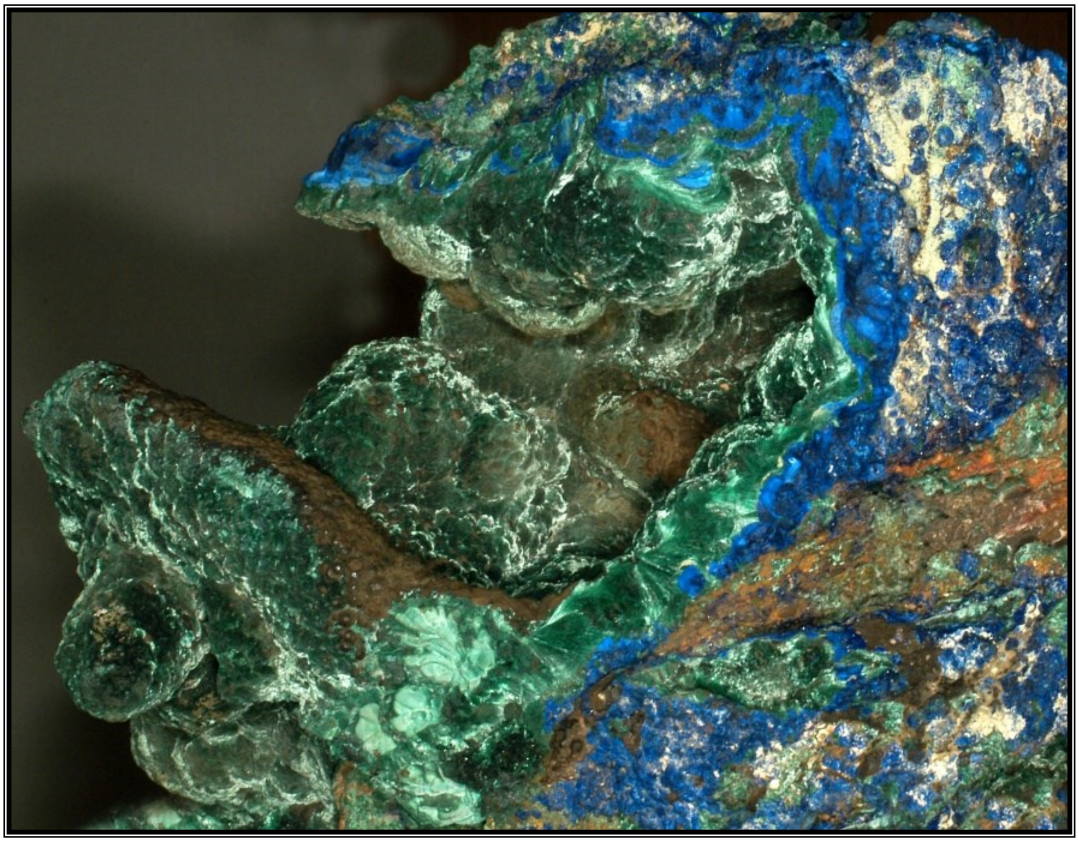


The large, 3.5-ton block of azurite, malachite and goethite in the American Museum of Natural History, 200 level, Czar Mine, View–1.6 meters. The photo is oriented to approximate the position, as found.

This unique specimen shows several features typical of in-situ, supergene replacement of a carbonate host rock. In this instance, Escabrosa limestone has been replaced in a subaerial environment preserving white chert fragments in their original orientation; folding of the beds and a minor offsetting fault remain evident. The abundant, though small voids reflect the loss and removal of sulfur and, to much lesser degree, iron.

An in-situ supergene deposit developed more-or-less in the locus of the original sulfide replacement deposit and was invariably relatively low in pyrite content. The depositing solutions could be characterized as indigenous, having originated at or very close to the point of deposition. Without abundant pyrite, the combined iron and other metal solutions have minimal geochemical mobility because of insufficient acidity. Thus, the immediately adjacent limestone is attacked with modest acidic solutions, quickly buffered, and carbonates formed. Some original limestone features are preserved, such as structure and encased chert, as shown in the above photograph.

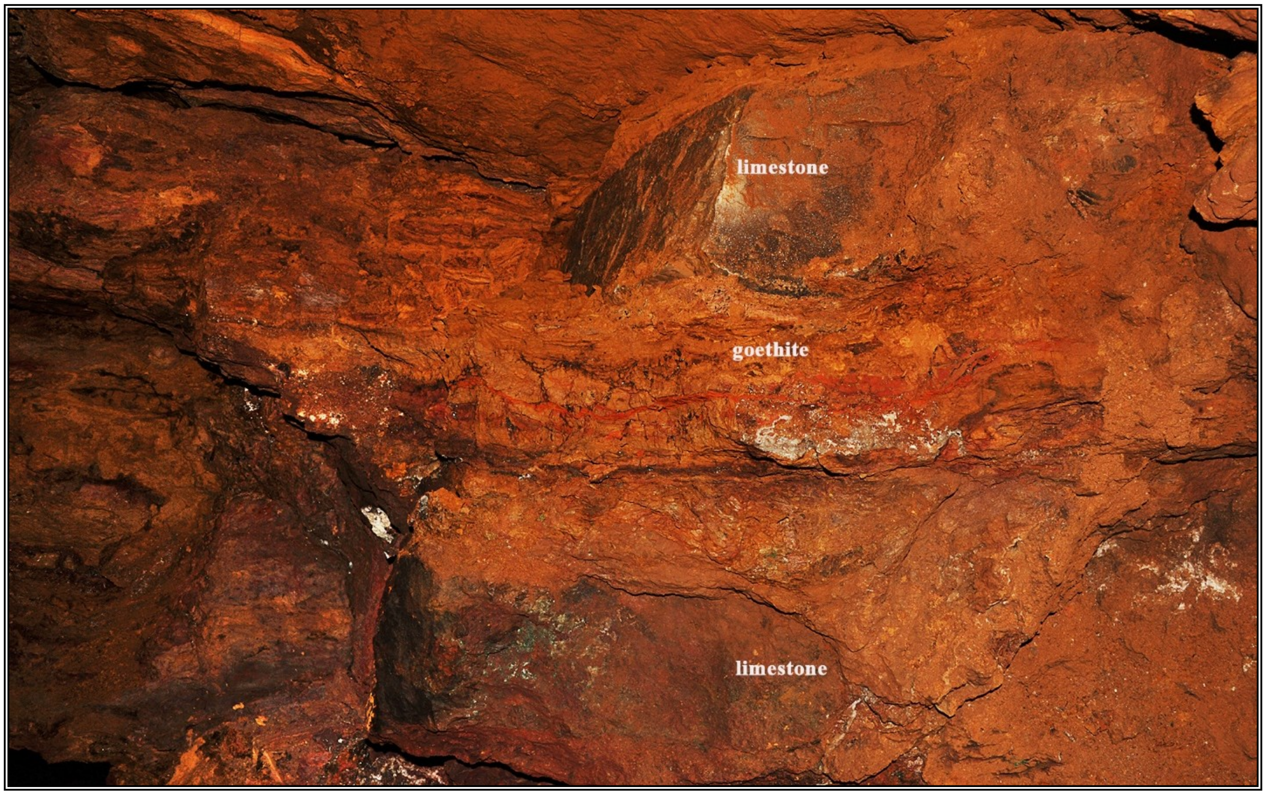
When the original copper sulfides were high-copper, such as bornite or chalcocite, massive malachite and/or azurite are deposited in situ with voids reflecting the volume reduction from sulfur removal. Usually, boxwork forms resulted, as the solutions followed the fractures in the hosting limestone. Little, if any, enrichment occurred, as the available copper in the solutions could not be greater than that in the original sulfides.



Malachite and azurite as boxwork with very minor goethite, reflecting the high-grade, low-iron of the original hypogene minerals. Note the stalactite in the lower-left corner which formed in a subaerial environment. Most of the malachite is a replacement of azurite, which was subaqueous in origin. Holbrook Mine – view-22 cm. Bisbee Mining and Historical Museum collection

Often, both subaerial and subaqueous events impacted some such depositional environments. To be sure, fluctuating environments were common during supergene alteration at Bisbee. It can be seen that both subaerial and subaqueous deposition took place in the large Holbrook piece with boxwork, illustrated above. It is manifested by the stalactite covered by azurite crystals of subaqueous origin, which have altered to malachite. Also, note the band of azurite, which was protected from alteration by later malachite deposition.

Massive pyrite, when oxidized more-or-less in situ and sufficient oxygen is available, would

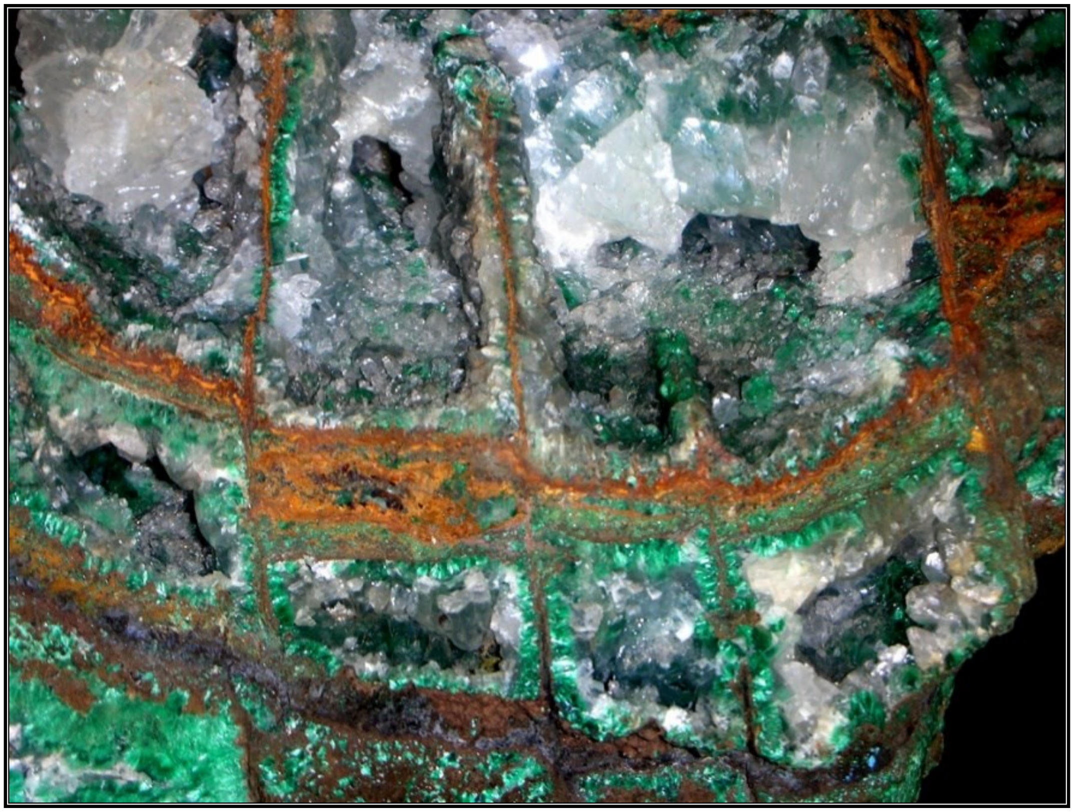


Massive bedded goethite deposited between limestone beds from the in-situ supergene alteration of pyrite in an oxygen-rich environment. Very little copper was in the pyrite. The horizontal stratification gives this a Pliocene or later age. 5th level, Southwest Mine, view–2.8 meters. Graeme/Larkin collection.

develop thick layers of goethite on corroded limestone from indigenous solutions, as illustrated above. The horizontal stratification was formed after tilting of the beds during the Basin and Range event, or post-Laramide.

Boxwork Forms:

Boxwork is the term universally employed to describe the generally rhombohedral/rectangular openings that form in carbonate rocks through the oxidation of sulfides and other near-surface weathering processes. These reflect the fracture pattern of the original carbonate. The development of boxwork texture in limestone by several carbonate species is well documented in many ore deposits worldwide. In this district, it was common and locally abundant. Boxwork forms were quite often the depositional sites for many of the supergene species. Indeed, a good many of the excellent Bisbee specimens consist of one or more copper minerals deposited in the boxwork voids or formed as boxwork. The voids ranged in size from just a few centimeters to 20-30 cm.



Goethite boxwork openings lined with malachite and calcite 3rd level, Southwest Mine – specimen-17.5 cm. Graeme collection.

Goethite was the most common mineral found as boxworks at Bisbee. Often, but not always, it was a replacement of earlier siderite. Malachite and azurite in boxwork form, while common, were far less abundant and usually as a coating on goethite. Smithsonite boxwork was locally abundant at Bisbee but even less common than the other carbonate minerals.

These all begin with the emplacement and subsequent oxidation of the primary sulfide replacement deposits. Emplacement of the sulfides was usually accompanied by intense fracturing of the host limestone. Large, low-grade, copper sulfide bodies were high in pyrite, which oxidizes readily when subjected to supergene processes. Large amounts of acidic, ferric iron-rich solutions were generated. These solutions followed the fractures in the limestone, dissolved it, and replaced it. The relic pattern of this fracturing is preserved by siderite or goethite boxwork.

The ferric ion is an oxidizing agent for sulfides, and in the presence of sufficient oxygen, goethite is the usual product. If, however, oxygen is not available, the ferric ion will be consumed, and an acidic solution of $Fe^{2+}(aq)$ will be preserved. As far as the limestone-hosted Bisbee ores are concerned, this would be simply achieved by the gas phase in the supergene zone becoming essentially 100% $CO_2(g)$ at the point of acid buffering. Considering the relative stabilities of calcite (limestone) and siderite, siderite is much less soluble than is calcite.

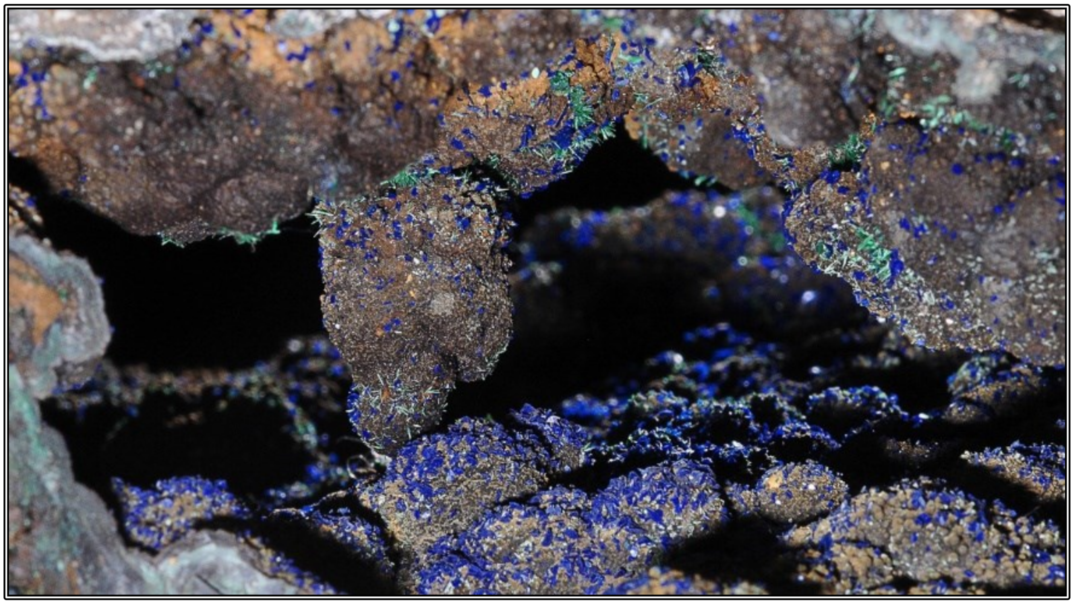
Early-stage goethite boxwork development in fractured limestone as thin parallel lines, which are siderite lined fractures 7th level, Southwest Mine. One of the authors, DLG. is in the photo. Graeme-Larkin collection.

With high $CO_2(g)$ and under ideal conditions, the calcite (limestone) will be dissolved, while siderite will remain as void walls. Oxidizing sulfides will generate significant acid that will attack limestone. As the partial pressure of $CO_2(g)$ builds up, oxygen will be exhausted, and $Fe^{3+}(aq)$ will be reduced to $Fe^{2+}(aq)$ via further reaction with sulfides. At this point, mineralizing solutions are necessarily at equilibrium with an exclusively $CO_2(g)$ atmosphere. Siderite replacement of limestone along joints and cleavages will proceed and, a further acid attack will preferentially dissolve the remaining limestone, resulting in the boxwork forms.

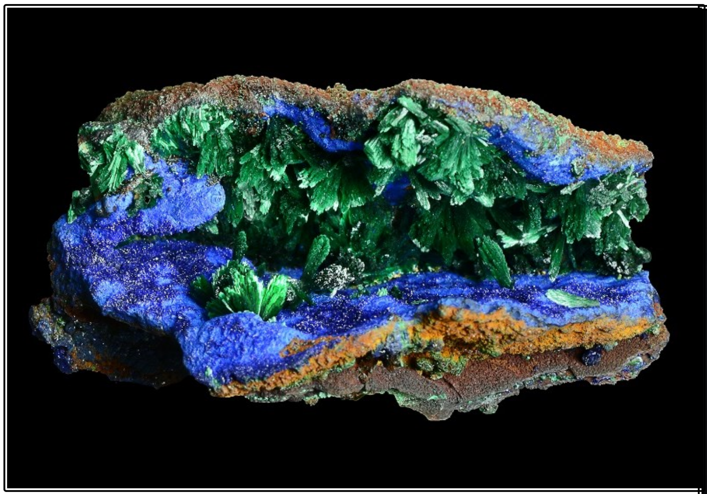
The very high CO_2 levels associated with some areas mainly composed of siderite were noted by Bateman et al. (1916). He recorded that in some instances, so much carbon dioxide was liberated when mining opened such a siderite area that it was necessary to remove the miners from the area for safety reasons because of the high concentrations of this gas (Bateman et al*.,* 1916).

With erosion, uplift, and/or faulting, the atmosphere would change to one more at equilibrium with the surface. However, sulfide oxidation continued, if not already complete. Further exposure to these acidic solutions and in an oxygen-rich environment would ultimately convert the siderite to goethite (Trischka, 1929). Goethite replacing limestone instead of siderite would be formed directly from the supergene fluids, as well, whenever sufficient oxygen was available.

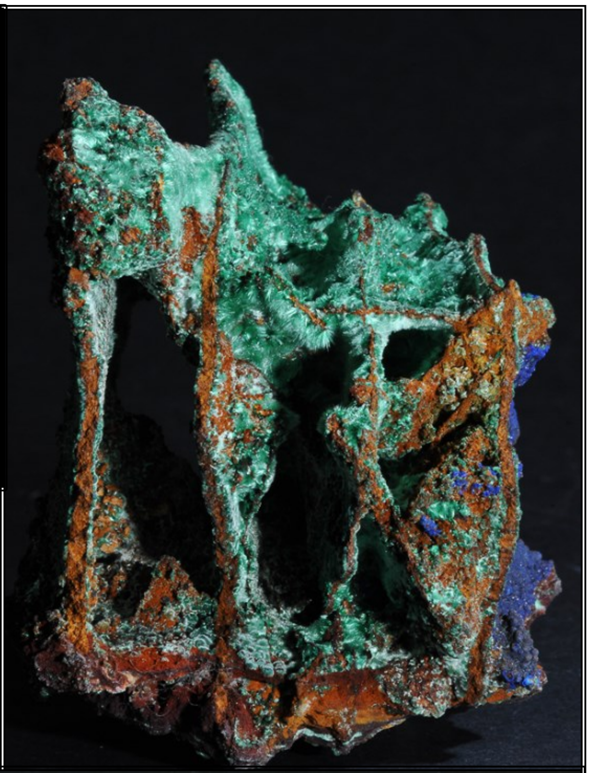
Siderite boxwork in-situ, 2300 level, Campbell Mine – view-1.50 meters. Graeme-Larkin collection



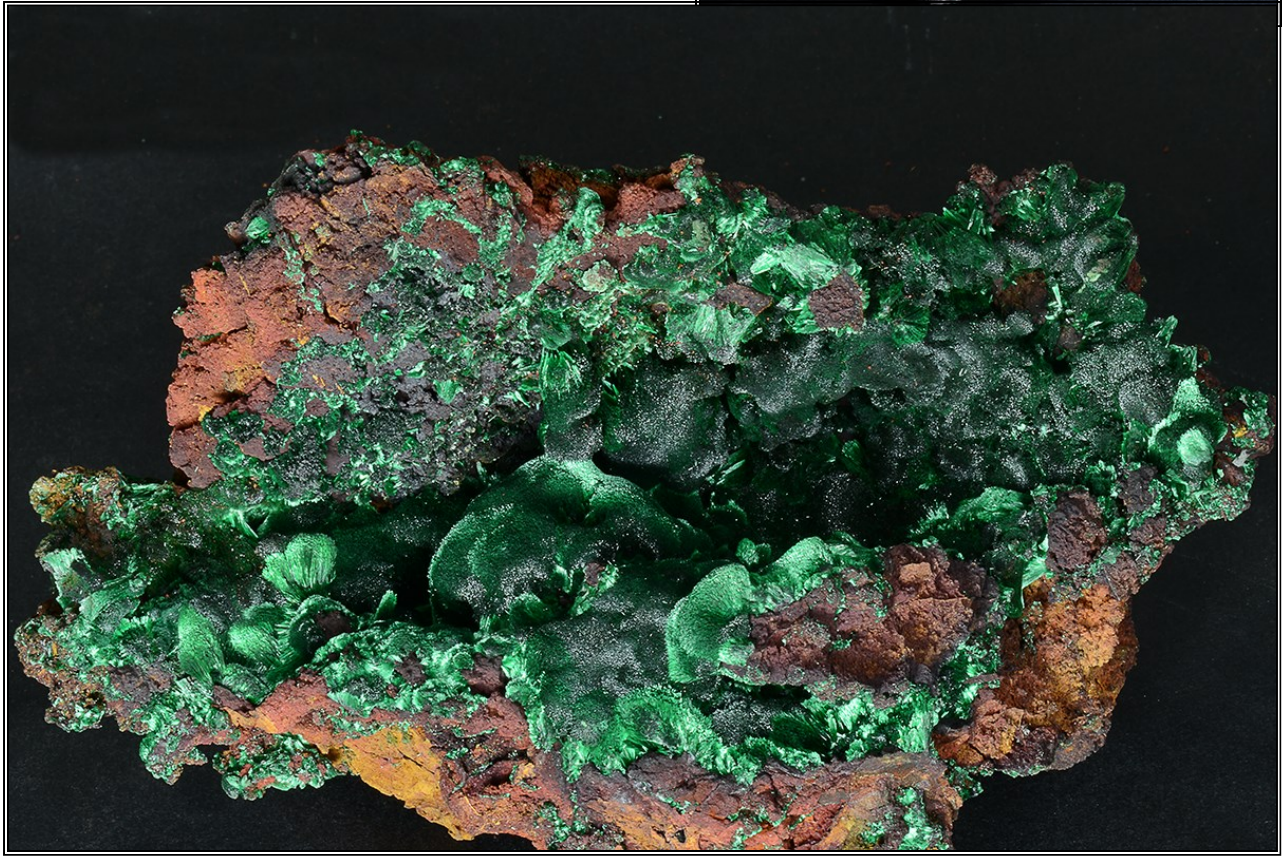
Goethite, as a replacement of and as pseudomorphs after siderite sprinkled with subaqueous azurite and minor malachite, 45 raise, 200 level, Shattuck Mine, View-8 cm. Graeme collection



Azurite with tufts of malachite both of subaqueous origin, in boxwork form goethite, Higgins Mine, Tunnel level, specimen-6.5 cm. Graeme collection. The azurite appears to have been partially reabsorbed during malachite deposition.



Goethite in boxwork form with malachite and minor azurite, both of subaqueous origin, Czar Mine, specimen-11 cm. Graeme collection.

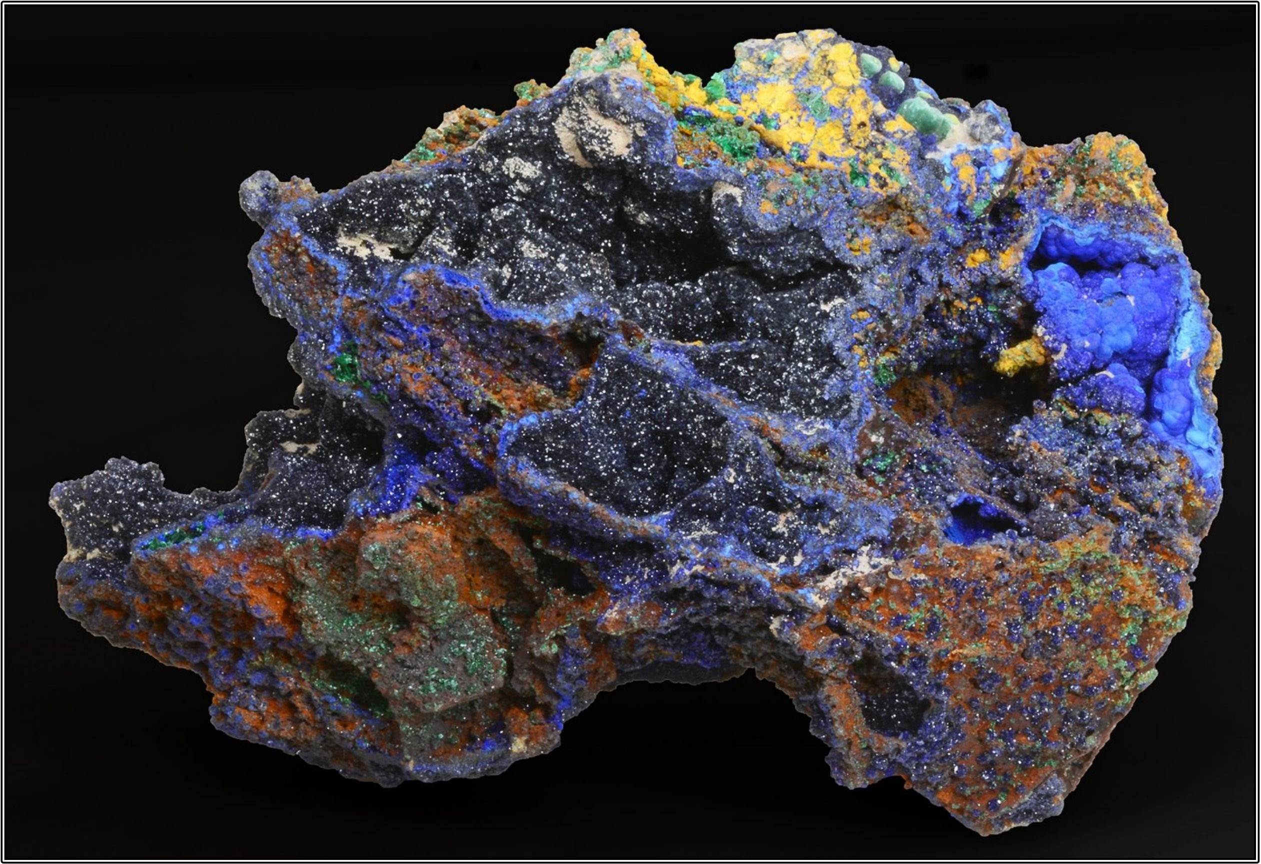


Goethite boxwork form with malachite of subaqueous origin, Czar Mine, specimen-17.5 cm. Graeme collection.

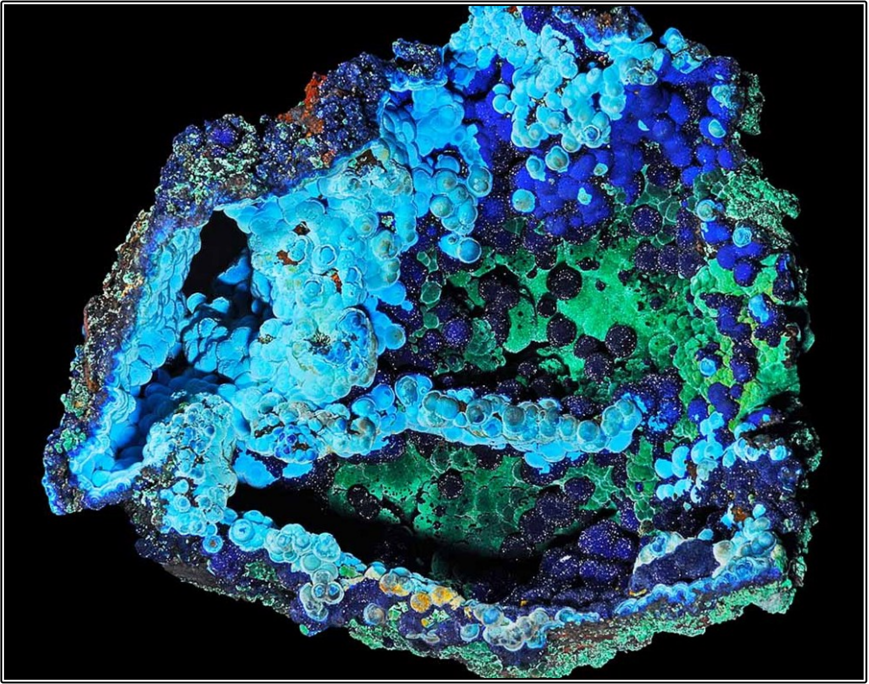
Goethite boxwork form with calcite overgrown on malachite. Some co-deposition of malachite with calcite is present as well, both of subaqueous origin, 5th level Southwest Mine, specimen-16 cm. Graeme collection.

Malachite and azurite in boxwork form, with little or no goethite, were usually formed nearly in-situ through the oxidation of high-grade copper, low pyrite deposits. Little acid was generated, and that available was quickly buffered along the fractures in the nearby limestone. Bornite and chalcocite were the main copper minerals in these types of deposits. Pyrite was usually present as well, but in relatively lower proportions than in other areas of the orebody.

The processes involved in forming azurite and or malachite boxwork were similar to those described above for siderite and goethite. The main difference was that substantially less acid was developed by the oxidation of these very high-copper minerals. Nonetheless, the available pyrite oxidized first, depositing minor siderite or goethite. The hypogene copper minerals in the deposit were more resistant to supergene activities; therefore, copper was mobilized later by the acidic solutions and at a much slower rate. If goethite was present, the copper carbonates were deposited on the goethite. If not, copper carbonate boxwork formed, removing the limestone for the same reasons as discussed for siderite, with available CO_2 driving the formation of the copper carbonate deposited. Boxwork malachite and/or azurite also occurred as isolated vugs at or very near the interface with the supergene clays and limestone, having retained the original form in the goethite now, very soft, from further oxidation with the copper carbonates protected by high CO_2. The encasing iron oxides were easily removed by simple washing. Often, the complete malachite/azurite lined void could be removed completely as a whole specimen.



Boxwork form azurite with minor malachite as well as goethite and hematite. Note: The light blue azurite was deposited in a subaerial environment, while the dark, crystalline material is of subaqueous origin, and coats earlier, subaerial azurite. Czar Mine, specimen-27 cm. Graeme collection



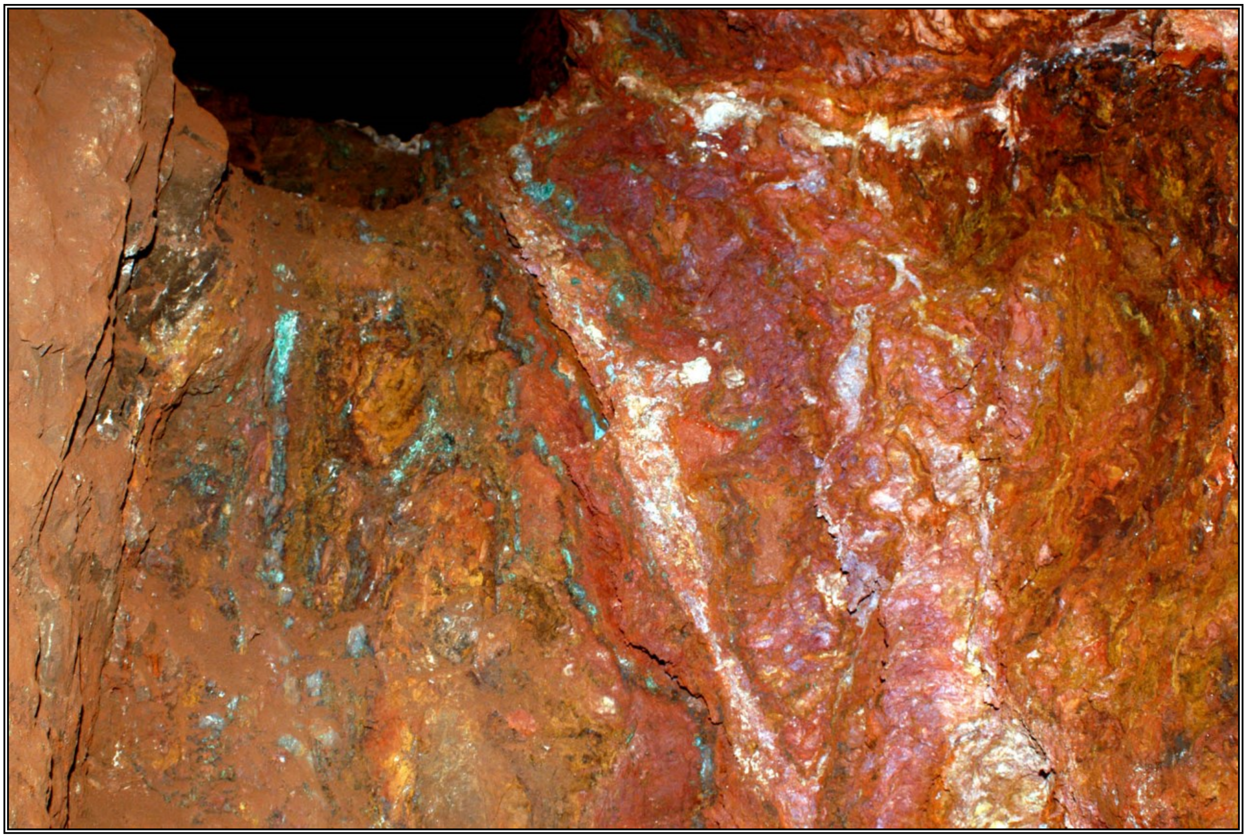
Right, Boxwork form azurite and malachite as well as very minor goethite and hematite. Note: Here too, the fine grained light blue azurite was deposited in a subaerial environment, while the dark, coarse grained, crystalline material is of subaqueous origin. Holbrook Mine, specimen-11 cm. Graeme collection.

This specimen represents nearly the whole of the vug, as only the lower portion was lined by the copper carbonates.

CLAY-LIKE ENVIRONMENTS

Many of Bisbee's fine mineral specimens were found in the enormous volumes of clay-like or clay-rich materials, which formed during oxidation. Douglas (1900) referred to these bodies as "ledge matter." Huge masses of clays were found in the western part of the district, with well over ten million tons found before 1900, as noted (Douglas, 1900). Much more of these clays were to be found in the subsequent years.

The claylike deposits were formed via the supergene alteration of hydrothermally altered porphyry, limestone, and soft supergene iron oxides, as alteration progressed. This gives them a mottled red-white-yellow-brown color and often a contorted appearance. Mineralogically, they were a variable mixture of several clays such as illite and kaolinite, claylike minerals, such as sericite (muscovite), halloysite-10Å, alunite, and gibbsite, with significant amounts of goethite, hematite, and manganese oxides intermixed. Often sticky and under pressure, they were a miner's hell, as they quickly closed workings, clogged ore transfer systems, and refused to be dumped, sticking inside the mine cars.



Ore grade supergene clay environment (right) grading into hard oxide ore, then into unaltered limestone, 5th level, Southwest Mine – view-2.5 meters.

These clays occurred in varying amounts in all of the areas that had undergone some degree of supergene activity. The more intense the degree of supergene alteration, the greater the relative volume of clays formed. In the western part of the district, which with four distinct oxidation events, had undergone the most supergene activity, the volumes were often stunningly vast and hard to mine, as noted. The seemingly constant movement of the mountain encasing the clays during mining created conditions of great concern. No matter how much support timber was placed or how close the backfill of mined-out areas, the rocks shifted to compensate – all the way to the surface.

Dr. Peter Williams (left) and author (RWG IV) in front of contorted, supergene clay ores, with cuprite as the principal ore mineral. Areas of cuprite altering to malachite and tenorite are indicated by the green areas. In 12 stope, 6th and 7th levels of the Southwest Mine, vertical view-about 10.5 meters. Graeme/Larkin collection.

It was only in the late 1930s that the face of Queen Hill seemed to stabilize, a genuine concern for the town. But then, this is about when mining in the Czar and Holbrook was ending.

When supergene copper minerals were included in these soft, plastic, sometimes almost fluid masses, they were an important source of ore. Elemental copper and cuprite were the most important ore minerals in these typically non-reactive environments, deposited by exotic solutions descending from above.

In general, but not always, the carbonate had been consumed during the supergene alteration process. However, some small, isolated patches of carbonate did remain and were quite common near the limestone interface. These latter occurrences were sites where often fine boxwork azurite and malachite specimens were found, as previously noted.

In the rest of these ore-grade clay masses, copper and cuprite were preferentially formed, in part, because there was not sufficient CO_2 available to react with the metal-bearing solutions, so copper simply precipitated from saturated solutions. Copper was found in sufficient amounts, often as very small, isolated copper particles (<2 mm), which were sufficiently disseminated throughout the material to make it of ore grade (7% copper or higher in sticky, unstable clays). Also, in these soft, typically plastic materials, copper less commonly occurred as more massive, free-floating, unconnected, usually crystalline masses, formed by the continual precipitation of copper from solution, thus enlarging some of earlier pieces, where the additional saturated solution was available. Modest amounts of cuprite were commonly associated species, usually as an oxidation patina or rarely coatings of tiny to small crystals, usually octahedra.

Copper simply precipitated from saturated solutions as isolated grains, growing over time. In general, because solution movement was severely restricted in the clays, a multitude of specks or small masses formed from a lack of additional solutions entering the environment to develop large masses or crystals. Though many did develop, these isolated masses would range in size from less than a centimeter to occasionally more than a meter across and several tons in weight. Smaller clusters of crystalline masses of less than 10 cm were far more common, indeed abundant.

To be sure, many large masses of copper did develop, as noted—some exceeding several hundreds of pounds (Douglas, 1900). We have seen a number of very large copper mass, including one of several meters in all dimensions, left in place because of the difficulty in mining pure copper. For the most part, however, it was the sum of the many tiny pieces that made the rock mass ore grade. These same localities always included the occasional, isolated larger piece (>10 cm) suspended in the clays. Any lump found in the soft mud/clay was probably copper, and generally, a simple washing would reveal a crystalline mass. Voids in the adjoining, altered rock would frequently host patinaed, free-standing crystals or crystal clusters lining the open space. In many instances, later calcite was deposited in the adjacent voids, but before the copper had acquired its patina and is bright within the calcite crystals. As a point of interest, this later calcite is invariably highly fluorescent, as discussed below.

The last all-elemental copper deposits mined in the late 1950s to mid-1960s were hosted by clay/claylike and massive, punky goethite. On the 2200 level Campbell, it took five-plus years to mine some 14,000 tons of ore that was made ore-grade by just native copper. No other copper minerals were recognized. This was mostly pre-Cretaceous in age and was less than 450 meters from the pre-Cretaceous paleosurface. A second, early Cretaceous event is evidenced by a later generation of small crystals preferentially oriented on the earlier, larger crystals' edges.

As this orebody had undergone only two periods of supergene alteration, much of the host rock had not been converted to clays. The lower portions were largely clay and contained some exceptional crystals, while the specimens from the upper areas were somewhat flattened small crystal masses, some of considerable size, reflecting boxwork forms in the hard goethite. A great many fine specimens from this type of locality are in collections today, as by then copper had gained some level of respect as specimens. Far more were saved than had historically been the trend.

At much the same time, several smaller stopes in the Cole produced some spectacular coppers from clays. In general, they were less than ten centimeters in size, and the clays were red to gray. Here the degree of oxidation was more intense than in the above noted Campbell occurrence but was less than the western area. The gray clays came from sandy facies of the Abrigo limestone and were difficult to clean. No other similar occurrence has been seen by the authors. The other stopes on this same level were in reasonably well-developed supergene clays, easily removed and cleaned.

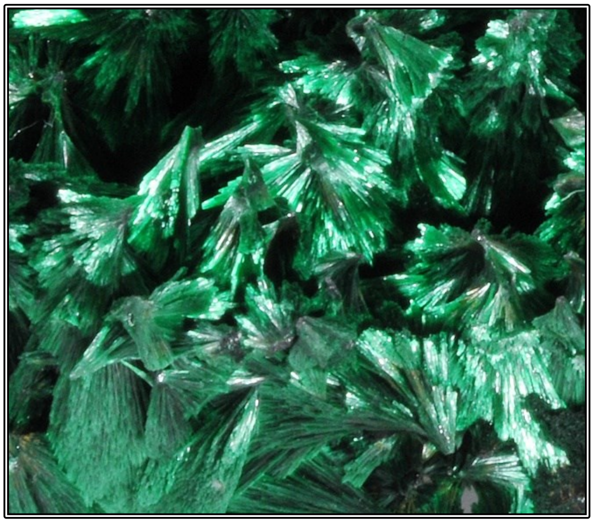
Cuprite was incredibly abundant in the copper-rich clays. In fact, it was probably the most economically important of the ore minerals for the clays, as anhedral blebs. When crystalline, the occasional isolated euhedral crystal to several millimeters and, on extremely rare occasions, to a centimeter were found encased in the clays. Almost all of the cuprite from the clays was octahedral or decahedral in form. In spite of its abundance, apart from the few noted euhedral crystals, good cuprite specimens from the clays are unknown. As a point of interest, the crystals illustrated were plucked from the clay during a lunch break in a contest to see who could find the largest "ruby" (Glenn O'Leary, personal communication, 1960).

Euhedral cuprite crystals to 1.4-cm, found suspended in soft, supergene clays. Holbrook Mine. BMHM specimens

Boxwork goethite on the margins of the clay masses were often sites for cuprite crystal development. These cuprites were formed by exotic fluids derived from the oxidation of sulfides some distance away in a nonreactive environment, one very low or free of $CO_2(g)$. The crystals were almost always octahedral in form, with cubes quite rare. There is no obvious reason for this difference in crystal morphology.

Cuprite nodules found in these clays often had exceptional crystals, Bisbee's best – always cubic, dodecahedral, or combinations of the two forms - but these are very different in origin, which will be discussed later.

COPPER CARBONATES IN CLAY-LIKE ENVIRONMENTS:



Right: Conical clusters of intergrown, acicular malachite crystals of subaqueous origin. The open spaces between clusters were filled with soft clays, which governed their growth. View-3 cm. Graeme collection.

Erratic carbonate masses, usually of small size, remained scattered throughout the supergene clays as a result of incomplete alteration. When contacted by low pH copper-rich solutions, they reacted to form either azurite or malachite, depending only upon the partial pressure of CO_2(g) and pH. In both cases, the copper carbonates deposited reflect a subaqueous environment, attesting to the soft, saturated nature of the clays, which were pushed aside by crystal development. Rarely were any of the clays captured as these grew, but small, pre-existing hard minerals, i.e., goethite chips or manganese chunks, may leave an impression but not be connected, while quartz fragments > 1

Three examples of malachite that grew in soft clays. Top left, highly lustrous mass of intergrown conical forms, Czar Mine, specimen-9 cm, Top right, radiating cluster of course, acicular malachite crystals. Sacramento Mine, specimen-7.5 cm. Bottom, Compact mass of radiating malachite crystals. The numerous, horizontal cracks reflect desiccation of the gel-like malachite following deposition. Czar Mine, specimen-17 cm, All from the Graeme collection.

mm from the decomposed porphyry and even a BB-sized spot of earlier, corroded malachite has been seen as inclusions.

Malachite that developed in claylike environments was an important source of ore and was very abundant as delicate, fibrous crystals as individuals, thin vein-like streaks, and as nests of acicular crystals to 7 mm. Even though this type of malachite was incredibly abundant, specimens of this type of malachite are uncommon, as they were delicate and usually poorly attached to the soft, friable matrix. Few were collected, and very few of these survived.

From a desirable specimen standpoint, there were the occasional tightly intergrown conical clusters of a centimeter or more long, lustrous, acicular crystals. These conical features were randomly oriented and form handsome, splendent, erratic masses up to 30 cm when the easily removed encasing clay is washed away.

As they were attractive and quite durable, a number were collected and preserved. If an open space was encountered during growth, a smooth surface develops on the malachite. It is not uncommon for bright, centimeter-sized, composite azurite crystals to be deposited later in this open surface.

Other malachite forms of interest from the massive supergene clays are relatively uncommon. Two uncommon examples are illustrated above, along with the more common small conical cluster type. In both instances, these are variations on the same form and suggest that more carbonate may have been available at the point of formation.

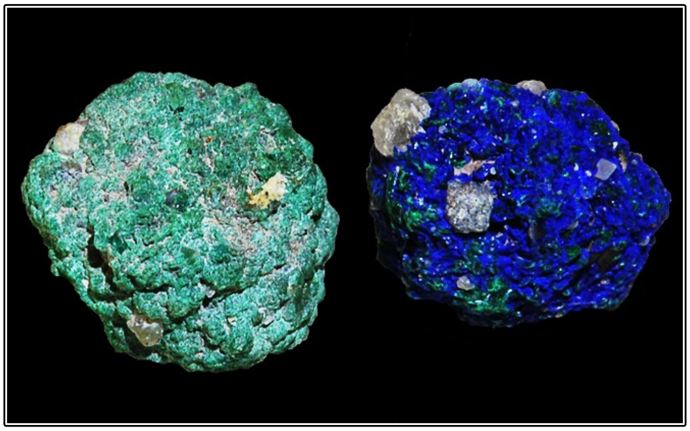
Malachite alteration replacements of/or pseudomorphs after spherical azurite forms were locally abundant. In the Holbrook Extension of the Lavender Pit Mine, many thousands of these malachite spheres ranging from a small dot to rarely, several centimeters were in the now-dry clays, reflecting ongoing supergene activity. With increasing depth, these graded into partially altered spheres and then into unaltered azurite, reflecting the depth of current supergene activity. We could easily see this transition in the recently blasted muck while mining.

Azurite sphere clusters from clays in the Holbrook Extension, Lavender Pit Mine. Left, as found with clay, 6.8 cm; right, a cleaned example, 7.1 cm.

Azurite as inclusions in the supergene clays was far less common than malachite but still abundant enough to make ore in parts of the western area. Just as with the malachite noted above, there were many thousands of spheres visible in the broken ore on several levels of the Holbrook Extension. However, while the plain malachite spheres were seldom attractive, the malachite sphere, which was a clear replacement of azurite and the unaltered azurite spheres were often handsome, and many were recovered.

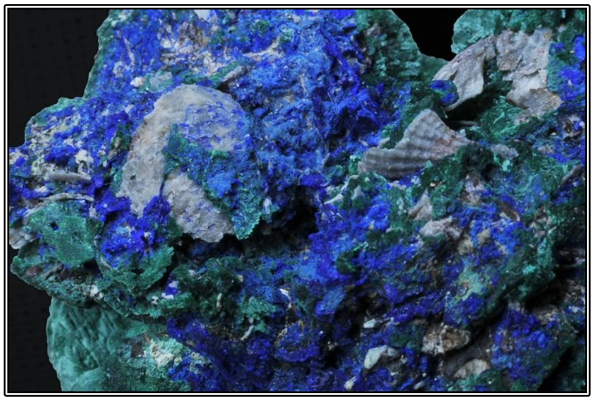
The azurite ranged from an almost electric blue to a nearly black hue of blue. The surface generally reflected tiny tabular crystals that have intergrown to form the rounded mass with varying degrees of luster. It was common for several individual spheres to be intergrown, forming a chainlike grouping or a cluster of randomly oriented spheres, as illustrated above.

Unlike other worldwide localities for such spheres, these were not attractive in any manner when broken. Most were solid azurite internally with a radiating pattern, a few were partially hollow, and others contained uninspiring malachite. When hollow, the openings were lined by pointed star-like voids, suggesting shrinkage from desiccation. The voids were lined with drusy azurite, reflecting their subaqueous origin.



Left: malachite replacement of an azurite sphere. Right, azurite sphere altering to malachite. Both with quartz fragments and each is approximately one cm in size, from the Holbrook Extension of the Lavender Pit Mine. Graeme collection.

Right: A 20 cm slab of sandy-clay with numerous azurite spheres to one cm. Holbrook Extension, Lavender Pit Mine. A pick mark groove in the center-right shows just how soft the encasing materials are. Graeme collection



Azurite, altering to malachite with silica fossil trash of Mississippian age. Found in massive clays, 800 level, Cole Mine, view-2.1 cm. Graeme collection

Another important locality for clay-hosted azurite/malachite masses was on and extending above the 800 level Cole, near the interior shaft. First discovered in the early 1950s, this locality was a prolific producer of striking and very desirable, rounded rosette-like azurite lumps to 7 cm composed of intergrown, 5 mm to 1 cm tabular crystals.

For the most part, these specimens lacked any luster but had great form and a brighter blue than most azurite specimens. Frequently these were partially altered to malachite, further enhancing their appeal. Many contained siliceous fragments of Devonian era fossils from the hosting Martin limestone.

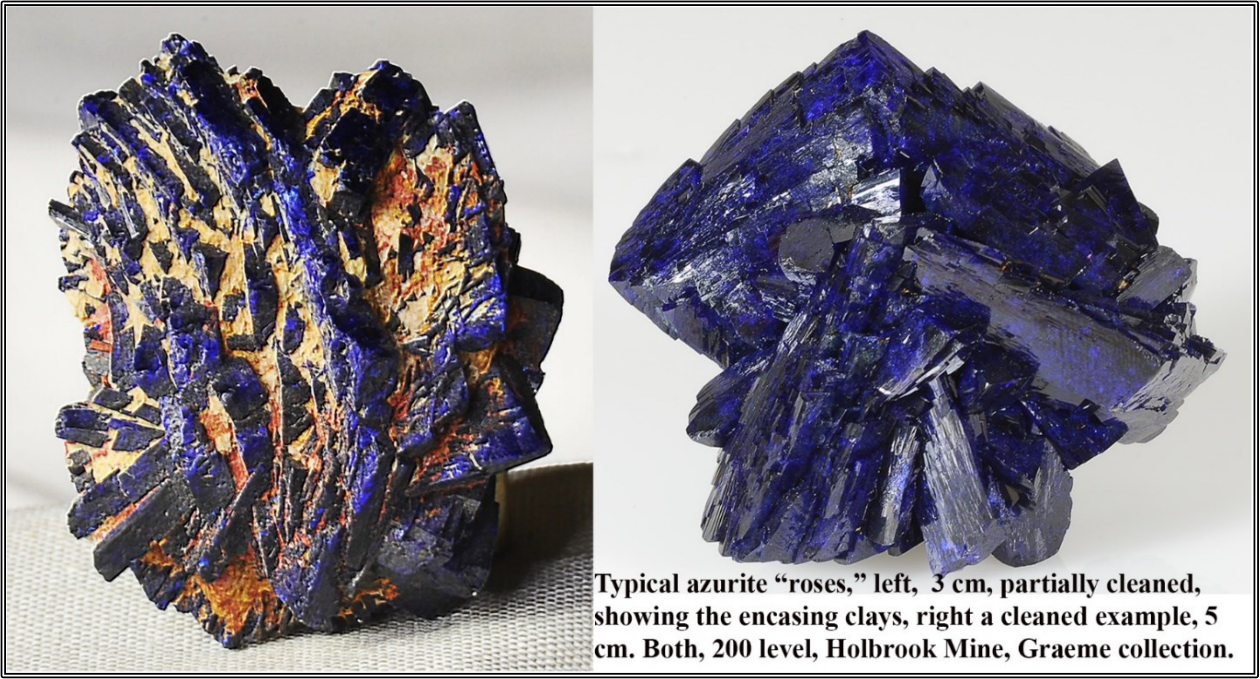
Given the relatively advanced degree of supergene-driven alteration, coupled with an understanding of the late-stage formation of other oxide ores nearby, these were most probably formed during the third supergene episode. The high degree of alteration to malachite of these specimens may well reflect the progressive alteration of the fourth episode.

The geologic setting where these interesting forms developed was very much like that of where Bisbee's best roses formed, though much smaller in area. These are discussed below. The principal geologic differences are that there is no apparent extension to the surface of the steep fault zone where they developed. Further, nearly 400 meters of rock cover are over this locality.

AZURITE "ROSES," A BISBEE CLASSIC:

For the purposes of this review, azurite roses are defined as highly crystalline masses with thick, intergrown, even blocky crystals forming all surfaces and which developed free-floating in soft clay and/or claylike material. They were never attached to a matrix at any time during their formation, other than another similar azurite form, or they may bear the impression of the iron/manganese clays in which they formed, essentially as "floaters." To be sure, other defining characteristics could be added, but these are, in our view, the more important. It is typical for near-spherical clusters of azurite crystals on a matrix to be characterized as rosettes, and this is an apt description. However, in keeping with the collector terminology as commonly used at Bisbee and generally elsewhere, these are not azurite roses. Examples of true azurite roses are figured below.

These roses, all of subaqueous origin, ranged in size from less than a centimeter to a very few as large as 10 to 12 cm. Most specimens seen in collections are in the four to six cm size range. Our experience suggests that a good many specimen of less than a centimeter were found but not collected. They were just too small for the collector's taste at the time. Perhaps one of the very few times azurite crystals were treated as just ore was when the tiny roses included in the clays and not readily visible were shoveled into the ore chute.



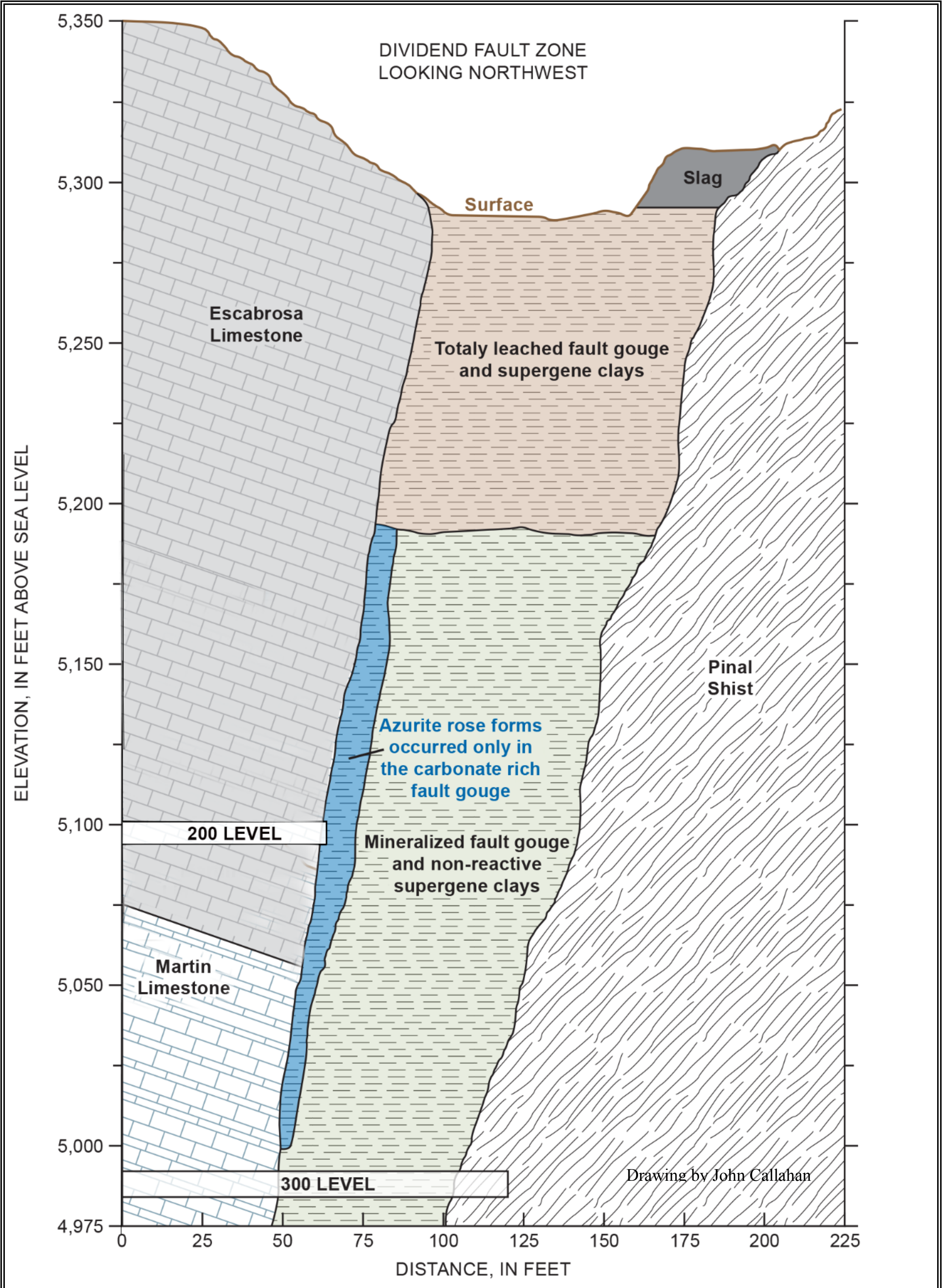
Typical azurite "roses," left, 3 cm, partially cleaned, showing the encasing clays, right a cleaned example, 5 cm. Both, 200 level, Holbrook Mine, Graeme collection.

Bisbee produced hundreds of superb azurite roses from the massive Dividend fault zone between the Czar and Holbrook mines. When these jewels were first found is uncertain, but the acquisition dates from several museums are as early as 1888 and 1889. The last roses to be recovered in volume were during the 1930s when leasers (lessors) last attempted to mine this treacherous area.

Mining the Dividend orebody was extremely difficult, costly, and dangerous. The ores were clayey, sticky, and wet with no rock strength. Scott (1919), in his discussion of mining the Dividend, noted that an opening made one day could be closed before the next because of pressure from the clays, and there was a very real risk of trapping miners. Fortunately, this never happened.

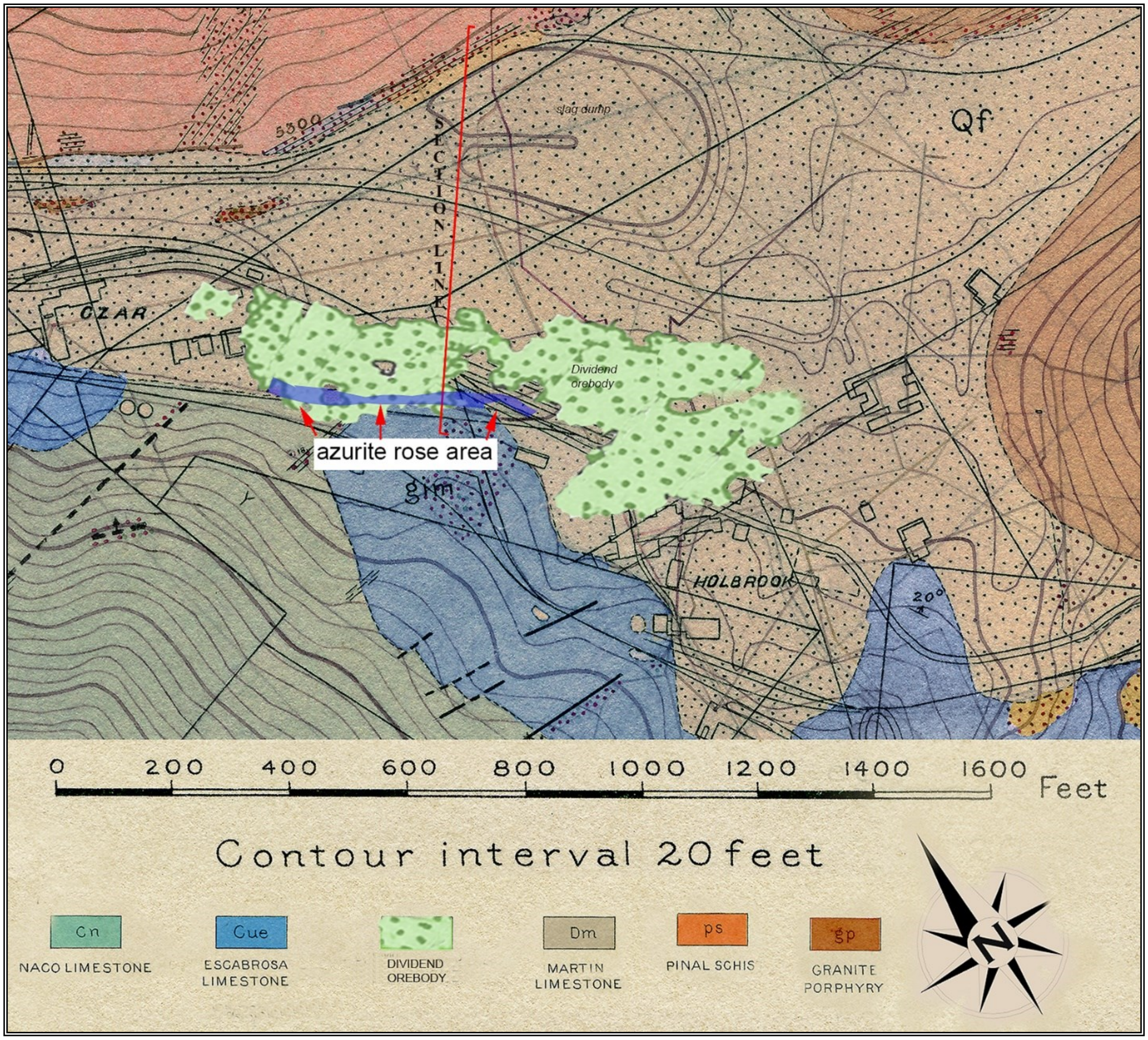
Nonetheless, repeated attempts were made over several decades; the rich ores were too tempting. With an overall grade of greater than seven percent copper and more than a million tons of ore, it was essential to learn how to successfully mine the Dividend ores. With repeated trials and, of course, errors, a safe and economical approach, called top-slicing, was employed. However, less than half of the ore tonnage was eventually recovered. The total costs of mining and handling these very troublesome claylike materials soon exceeded their value as ore. Ore reserve maps from 1941 in the author's collection show substantial reserves still in place.

Azurite was but a very small portion of the Dividend ores, with supergene chalcocite and lesser amounts of bornite suspended in the clays providing most of the copper. Roses occurred only in a narrow band along the hanging wall from just above the 100 level (≈ 30 meters below the surface) to almost to the 300 level (≈ 95 meters), but the Dividend orebody extended from 15 meters below the surface in some sections to the 500 level (± 150 meters) in depth at its deepest point. The roses appear to be restricted to the lower Escabrosa and the upper Martin limestone horizons.



GENERALIZED SECTION OF THE DIVIDEND FAULT ZONE
APPROXIMATELY MIDWAY BETWEEN THE CZAR AND HOLBROOK SHAFTS

Abundant, claylike fault gouge, which was very plastic, if not fluidlike, is key. To illustrate those features, as found at Bisbee, a generalized cross-section is included above. The 200-mine level reflects the Czar access, while the 300 level is from the Holbrook. An approximate location of the cross-section is indicated on the following surface geology map with a red line.



A modified clip from a 1909 Copper Queen Consolidated Mining Co. geologic map showing the limited area where limestone is present in the Dividend hanging wall, while weakly mineralized Pinal schist forms the foot wall. A vertical projection of the Dividend orebody has been added, as has an indication of the approximate location of the cross section.

The Dividend fault extends for miles. It served as the conduit for the several intrusives of the Sacramento Stock Complex and the mineralizing fluids, perhaps even the Juniper Flat granite. Bisecting the Mule Mountains, it formed the canyon that holds Bisbee. However, just two kilometers of this massive fault were mineralized, and only 200 meters of this structure hosted the conditions which allow for the formation of azurite roses.

Over the near-century of mining at Bisbee, azurite “roses” were found in a number of different localities, though only those from the Dividend were truly great. We have collected roses in six spots in Bisbee, some broad in extent, but most were small in area. In all instances, the general geologic environments were the same.

Further, we extensively collected azurite roses in the Hanover Mine in Fierro, New Mexico, when working at this mine. Using our understanding of the geologic controls, we successfully collected numerous copper pseudomorphs after azurite from the Copper Rose Mine near Hanover, New Mexico. These latter two localities exhibited identical geologic characteristics to the Bisbee localities.

The geologic features that all the sites have in common:

- High angle fault, normal or reverse
- Carbonate rocks in hanging wall
- Nonreactive, mineralized footwall rock
- Supergene copper sulfide mineralization in the fault gouge

While small occurrences of azurite roses at Bisbee were noted in several places, only two were of any real significance, and only the Dividend occurrence was truly great. The Campbell fault on the 1800 level of the Campbell Mine produced a good number of rose forms, some of which were very fine - large, lustrous, and a pleasing blue hue, not the near-black such as those from the Dividend fault zone in parts of the Czar and Holbrook Mines. The Dividend roses are the best found anywhere, helping to make Bisbee famous for extraordinary azurites.

We believe the azurite roses from the Dividend fault zone are geologically young, perhaps very young. Unlike much of the azurite from anywhere else in the district, these azurites show no alteration to malachite, such as that caused by diageneses, which occurred district-wide during Cretaceous times. Even later alteration through proximity to the surface is not present. Yet, the uppermost roses were little more than 30 meters from the surface and underneath the main drainage for the east flank of the Mule Mountains. This strongly suggests a very late-stage formation and/or isolation from oxygenated groundwater. Fewer than six malachite pseudomorphs after the rose form of azurite, which are reportedly from Bisbee, are known to exist. Unfortunately, the absolute origin for all is uncertain.

Interestingly, no other azurite or malachite formed in the limestone hanging wall, suggesting all of the available Cu in solution had been complexed before reaching the solid limestone. This is consistent with our observations at other azurite rose localities.

Using the continuity of the supergene chalcocite enrichment blanket in the porphyry units on both sides of the Dividend fault and the Pinal schist, Cook demonstrates that there was no Miocene or later movement along the fault. However, supergene activity was underway, as he dates alunite from the footwall side at 9.08 Ma (Cook, 1994). We know from the high-iron water issuing from a spring near Sacramento Hill, supergene activity was ongoing at the time of discovery (Cox, 1938). Paleoclimate data from the Pleistocene era for southern Arizona indicates an extended period of heavy rainfall, which would have accelerated supergene activity as well as mechanical weathering along the trace of the Dividend, given the severe topography.

This was followed by the current arid conditions, which is creating conditions where mechanical weathering (erosion) outpaces chemical weathering (supergene activity). This would be especially true for the soft fault gouge along the trace of the Dividend fault. Thus, little of the easily eroded leached fault gouge covering mineralized material remains.

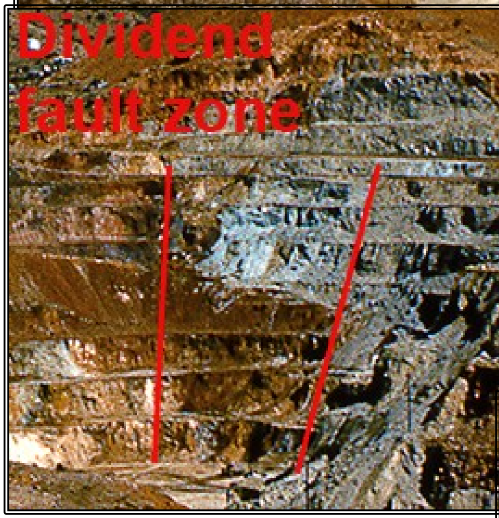
Nonetheless, the ±20-30 meters of totally oxidized supergene clays and mineralized fault gouge above the zone liberated substantial copper sulfate solutions, as the sulfide ore minerals were chalcocite and bornite, both quickly mobilized in an advanced supergene environment. If the permeability along the limestone hanging wall was higher than the clay-filled fault zone, as is typical, these solutions could have formed the roses. Clearly, abundant carbonate in the limestone-derived fault gouge along the hanging wall drove the formation of azurite through the high pCO_2 generated during the reaction between the acidic solutions and the carbonate. It is probable that the resultant, partially buffered solutions were near the lower pH range for azurite formation (3.4-4.5).

Speculative, to be sure, but Scott (1919) wrote that the higher grades were along the hanging wall and decreased as the footwall was approached. This suggests the copper in the fault gouge near the limestone /porphyry hanging wall was enriched, possibly by preferential supergene fluid flow along the hanging wall, which was less impeded by the clay/claylike mineralogy. The footwall was the clay-forming Pinal schist, which was often impermeable.

The reasons for the seemingly well-defined vertical limits are not totally clear. The upper limit was very close to the water table at the time of early exploitation. The total consumption and destruction of any carbonate available are to be expected at the upper extent; above the redox boundary (reduction/oxidation) boundary at or above the water table in an acidic supergene environment with the metals transported downward and redeposited, usually as sulfides, unless carbonate was available.

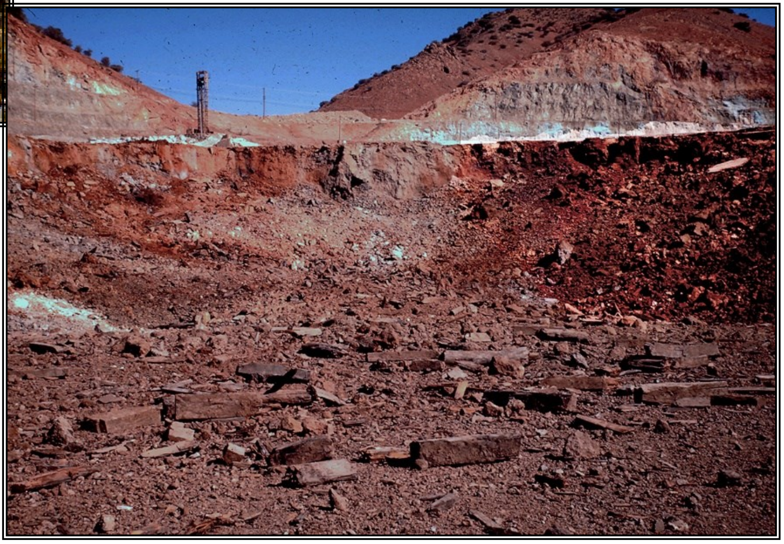
This boundary shifted over geologic time with burial and erosion. However, it was probably relatively stable over recent times and during the formation of the azurite roses. There were substantial amounts of buffering capacity along the hanging wall, and the pH of the solutions was probably moderately low, given the abundant sulfides in the fault gouge. This would preferentially form azurite. Below the water table, the deposition of a different suite of secondary copper minerals could result as a function of the Eh and pH while depositing copper minerals with variable copper to sulfur ratios with carbonates possible until the available CO_3 and CO_2 were consumed.

The lower extent may well reflect the depth to which the low pH, copper-rich solutions have been buffered. The amount of buffering material available may have been very low, with substantially less limestone in the gouge. The lower gouge content of CO_3 was possibly a function of the underlying Abrigo limestone, which is far less pure than either of the overlying units and was also much more susceptible to alteration during intrusion/ mineralization.



Above, the Holbrook Extension of the Lavender Pit in 1970, with the Dividend fault zone outlined. In the centerground, is the material from the Spray slope failure, which was largely removed later to continue mining. Graeme/Larkin collection.

Left, the Dividend fault zone from the above photo enlarged.

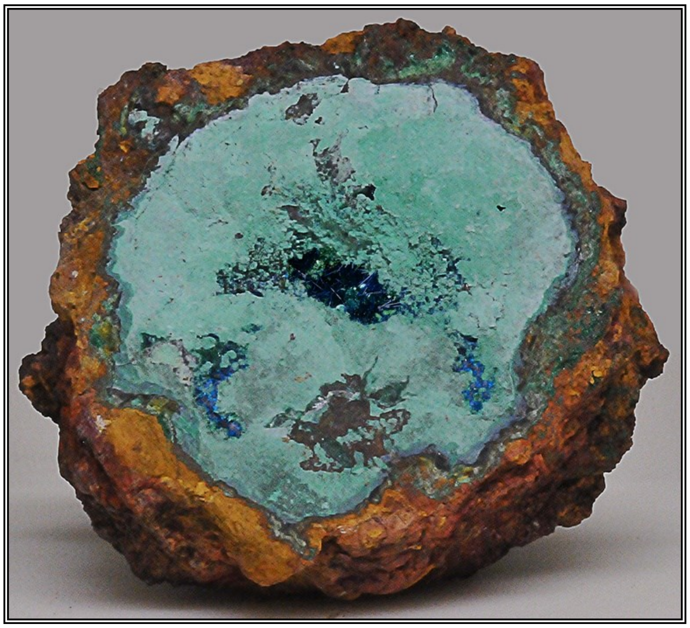


Right: After a blast of the hematite-rich, Dividend orebody area filled with alteration derived clays; April 1970.

For scale, the mast of the drill on the level above is 20 meters tall. This pit level corresponded to about the 200 level Czar. Note the lack of large rock fragments. Most of what appear to be large rocks are clumps of clay.

The scattered timber was support timber installed during underground mining. Graeme/Larkin collection.

CUPRITE NODULES:



Cuprite nodule with a surficial coating of paratacamite. Connellite and claringbullite are in the vug. The goethite rind is typical. 5th level, Southwest Mine, specimen-15.5

The term “cuprite nodules,” as used here, is somewhat loosely employed to describe the generally rounded cuprite masses that were so common in the clays associated with many deeply oxidized orebodies in the southern and western parts of the district. These masses were often the host sites for many of the rare or unusual supergene mineral species for which Bisbee is so noted. The nodules all appear to have been a very late-stage feature of the multiple supergene episodes.

Masses of near-pure cuprite were commonly found in many of the oxide deposits as a minor part of the ore mineralogy in all but the eastern part of the district and were most common in the western area. They usually occurred as isolated, typically rounded individual masses that ranged in size from just a few tens of grams to the occasional mass that exceeded 20 tons. Most were less than a few kilos in total weight, however. Economically, these nodules were not particularly important, but they are fascinating from a mineralogical standpoint.

Not all or even most oxide orebodies hosted these masses, but when present, they would be relatively abundant. These were formed in the ubiquitous, soft, non-reactive, iron-rich clays that developed during the supergene alteration in areas where the partial pressure of CO_2 was low and insulated from the hosting limestones by distance or impermeable clays. They are undoubtedly the residual, in-situ supergene alteration product of very high copper hypogene sulfide minerals such as chalcocite. Many of the unaltered sulfide orebodies contained isolated masses of near pure chalcocite, usually included within other primary sulfides. It is these masses that appear to have been the source of the cuprite nodules.

In a mixed hypogene assemblage, chalcocite is typically the last sulfide to be altered under supergene conditions. Absent abundant solutions to carry the copper away, it was deposited in situ. Schwartz (1934) noted massive cuprite, which had formed as a direct, in-situ alteration product of chalcocite, something we too have seen and sampled, but not in a cuprite nodule forming environment. The voids commonly found in the nodules reflect the removal of modest amounts of sulfur during oxidation, as would be the case for chalcocite, which contains relatively low sulfur and no appreciable iron. Relic textures and/or inclusions of unaltered, hypogene minerals such as residual, primary cassiterite, which survived supergene alteration, can occasionally be found in these masses, just as it can be found, on occasion, in chalcocite, further confirming their origin.

Cuprite nodule in-situ, 14 stope, 5th level, Southwest Mine – view-1.2 meters. A U.S. 25-cent coin (25 mm diameter) is placed for scale. Graeme/Larkin collection

When found, the cuprite nodules always had some degree of an alteration rind around their exterior and, to a lesser degree, along fractures. The rind consists of an exterior layer of goethite and/or chrysocolla (much of which was black and strongly resembled tenorite), then malachite, and finally with tenorite immediately next to the cuprite. This reflects the increased partial pressure of CO_2 that causes malachite to form. A subtle interplay of chemical and physical factors is involved with the development of chrysocolla, goethite, and or other minerals. Complete alteration of the cuprite to malachite was quite common. Less common was a complete replacement by chrysocolla or goethite.

Vugs hosting well-developed cuprite crystals, which were always in cubic, dodecahedral, or a combination of these forms, were frequently found in these nodules. The very best of Bisbee's fine cuprite specimens, all cubic in morphology, came from these vugs in the western part of the district.

A number of species are associated with this type of cuprite occurrence, and many have been found only in this type of environment at Bisbee, usually as the complete filling of small voids. For the most part, the mineral species that have been found only in cuprite nodules are rare, if not very rare. The reason for the close association of these minerals with cuprite is unclear.

Cuprite boulders and nodules form the matrix and provide the protection of the anomalous suite. This protection as provided by the cuprite envelope is supremely important. No doubt, the non-reactive, closed microenvironment of the nodules allowed the copper to complex with other available ions. If it had not been encapsulated, subsequent reaction to form more common species would have occurred as mineralizing solutions took on a more normal composition.

The table presented below lists the minerals recognized in direct association with the cuprite nodules. For the purposes of this discussion, the relative abundance of these species is noted only as they have been found either in the cuprite nodules or within the alteration rinds so common to these masses. This list is intended to serve as a guide to cuprite nodules and not the relative abundance of a species district-wide.

COMMON	RARE	VERY RARE
goethite	atacamite	claringbullite
hematite	paratacamite	paramelaconite
calcite	clinoatacamite	tolbachite
chrysocolla	connellite	graemite
malachite	bromargyrite	teineite
tenorite	chalcophyllite	nantokite
copper	buttgenbachite	likasite
brochantite	antlerite	botallackite
azurite	spangolite	ralstonite
	miersite	spertiniite
	minium	eugenite
	chalcoalumite	gerhardite
		bandylite

Table 9: Mineral species found in association with cuprite nodules

Very few cuprite nodules contained one or more of the rare or very rare minerals, as listed above. The presence or absence of these rare minerals was not consistent in cuprite nodules, even throughout an individual orebody. Nodules from the same orebody would host different assemblages, even when the nodules may have been less than a meter apart. Usually, the nodules were barren, except for cuprite crystals.

We have sat in more than a dozen oxides stopes in the western and southern parts of the district, breaking any number of nodules in the search for these minerals, and would only find something in one of 30-40 or more. A Volkswagen-sized boulder and several other five to ten-ton boulders from the Holbrook Extension of the Lavender Pit Mine were reduced to very small pieces by us, finding only small amounts of exterior chalcoalumite as a very late-stage alteration feature formed at the expense of the cuprite. A good many void from the boulders were lined with clean, bright, 6 mm dodecahedral and less often cubic crystals.

Part of a cuprite nodule with connellite and a single atacamite cleavage face and goethite, 1200 level, Cole Mine – specimen-4 cm, Graeme collection.

When any of the rare minerals were present, they most often occurred as small, included patches that completely filled voids in the massive cuprite and/or along fractures. On rare occasions, they occurred as small, freestanding crystals in vugs within the cuprite. If several species were present, one would be decidedly dominant. Connellite was far and away the most common inclusion found and was often the only accessory mineral present in the cuprite. It is possible that some of the material identified as connellite is actually buttgenbachite, which is visually indistinguishable. Connellite is classed as sulfate and is hydrated copper sulfate chloride hydroxide, while buttgenbachite is subclassified as a nitrate with a composition as hydrated copper nitrate chloride hydroxide.
Though much less common, paratacamite is the second most frequently found species but a very distant second.

Given the occurrence of these minerals as inclusions within massive cuprite as void fillings and along fractures as well as crystals in vugs - all within the same nodule, clearly suggest that they developed following cuprite formation. What happened in these little reaction vessels (the open spaces) is unclear, as is the source of some of the components. The metals are easily accounted for, given the complex mineral assemblages in the hypogene ores, but the nonmetal ions source challenges the imagination. Where did the chlorine come from? Even more puzzling is the nitrate.

While the amount of chlorine typically required is quite small, there is no obvious source. In general, other chlorine-bearing minerals not associated with cuprite are somewhat uncommon in the district but are widely spread, including in the eastern and mid areas. Chlorargyrite is the most common and is locally abundant in the eastern part and to a much lesser degree in the southern and western areas. Murdochite is the only other recognized chlorine-bearing supergene species and is found only in the western area and is not particularly abundant. Even atacamite and related species are uncommon at Bisbee unless cuprite is also present.

Did the chlorine come from fluid inclusions in the hypogene ore minerals or from a surface source, like saline ground-waters, such as seen in Western Australia (Peter Williams, personal communication, 2005), or was there some other source? Chlorine is quite reactive and cannot be expected to have traveled far before complexing in an active supergene environment or to have survived multiple episodes of supergene alteration unless isolated; perhaps this is the answer.

First, a look at other possible options. The vertical extent of supergene, chlorine-bearing minerals in the cuprite nodules is about 240 meters, from between the 1200 level Cole to above the 5th level Southwest with no consideration of the paleosurface, as there is no post-ore cover present. The horizontal distance exceeds 1.5 kilometers, but there are cuprite nodules at varying depths in the scattered, isolated oxide orebodies all along the way. None of these orebodies are connected in any manner, and the sharing of fluids is highly improbable, yet chlorine minerals are present.

There is no evidence of saline ground-waters, such as seen in Western Australia, but none would have survived the massive solution movement through the ores undergoing oxidation. Should the early-Cretaceous flooding by shallow seas be considered? There is reason to suggest that the relatively abundant chlorargyrite in the partially oxidized ores in the eastern and a small part of the southern areas are from the second supergene episode, which occurred when the whole area was covered by this inland sea. Thus, they may owe their origin to a chlorine-rich submarine environment, which is speculative to be sure.

All of the halogen elements have been found in varying cuprite nodules, albeit, in minuscule amounts, with bromine the second most abundant. Iodine and fluorine minerals are present but ever so rare. Fluid inclusions in the original ore minerals may be the source of these. The needed volumes were potentially available, and this seems to be the more probable source, but this is still little more than a well-considered guess. Residual, captive solutions from the above-noted seas need to be considered as well.

Another quandary, several of the species found in the cuprite nodules contain nitrate, though they are uncommon. Species such as buttgenbachite, gerhardite, and likasite have been identified, with buttgenbachite the most common and may well prove to be widely distributed, as more of the material identified as “connellite” proves to be buttgenbachite. For these minerals, the source of nitrate is, in our view, uncertain.

Melchiorre and Talyn (2014), using isotope analysis on material from the Cole Mine, suggest that guano is a possible source of nitrogen. We have trouble rationalizing this source. Given our intimate knowledge and understanding of the deposits, we can place most areas into a generalized three-dimensional consideration, thus relate the whole of the surrounding area to the occurrence. To us, guano seems an unlikely source.

The integral role of bacteria in the supergene process is well known. With no other source of nitrogen obvious, it could be speculated that for the very little nitrate present, a microbial source is possible. Not nitrogen-fixing bacteria, but merely the organic residue from bacteria present during bacterial-driven oxidation by acidophilic iron-oxidizing and/or sulfate-reducing bacteria.

Enders (2000) gives an excellent summary view of the bacterial role (*Thiobacillus ferrooxidans)* in supergene activity in Morenci. Further, with Melchiorre (Melchiorre and Enders, 2003), discussed how carbon from the remains of *Thiobacillus ferrooxidans* contributed to the formation of azurite at Morenci. It is not too great a leap to suggest the NO_3 needed to form nitrates at Bisbee came from the same organic source. This is a research opportunity to better understand the many, as of yet, unrecognized impacts of bacteria in mineral formation.

Bisbee’s cuprite nodules formed as individuals in isolation in low CO_2 ($p(CO_2) > 10^{-1.36}$), as set out earlier), surrounded by largely impermeable supergene clays with massive, nearly pure chalcocite, as the chalcocite was originally deposited as scattered masses in the sulfide ores.

Hypogene chalcocite is typically the last copper sulfide to decompose under supergene conditions; thus, any reactive minerals adjacent to the chalcocite had been consumed by earlier reactions. The common formation of supergene clays insulated the in-situ alteration of chalcocite to cuprite. Most of the elements included in the original chalcocite remained, often with relatively abundant chlorine, to form the anomalous minerals. Occasionally minor amounts of nitrate were captured as well, forming the more unusual of the anomalous minerals. These grew in, if not filled, voids formed through a reduction in volume caused by sulfur removal. The massive cuprite, in turn, provided a reaction vessel for the formation and a protective envelope for the anomalous suite of minerals, including connellite, spangolite, claringbullite, etc., as well as the nitrate-bearing buttgenbachite and gerhardite.

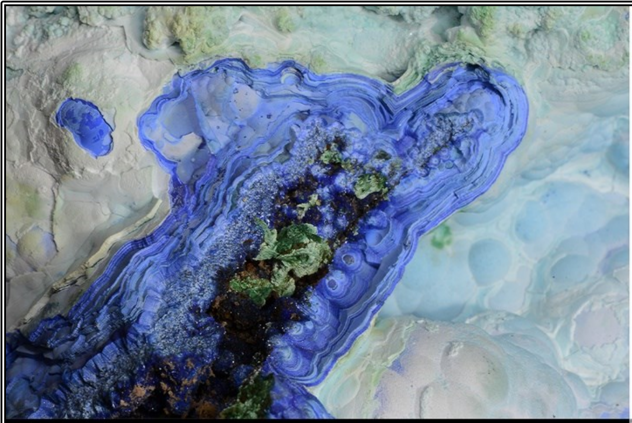
A complex group of rare minerals from a cuprite nodule vug. The dominate species is paratacamite, followed by spangolite and atacamite. Exceptionally large (6 mm) blue/green claringbullite crystals are spotted with connellite, all on cuprite. 5th level, Southwest Mine, specimen-4.5 cm. Graeme collection

Supergene activity continued at Bisbee, slowly altering these cuprite nodules. The complete alteration of the cuprite to malachite was common, less so was the alteration to chrysocolla or goethite, but none of the rare or very rare minerals as listed above survived total alteration. These species, which occasionally did survive some degree of alteration, are few in number. A small few are known where they occurred in goethite, which was derived from cuprite. Replacements by and pseudomorphs of malachite after atacamite, brochantite, connellite and have been recognized in specimens of altered cuprite.

ALUMINUM FLOODING AND THE FORMATION OF CHALCOALUMITE:

Bisbee is the type locality for chalcoalumite a basic hydrous sulfate of copper and aluminum ($CuAl_4(SO_4)(OH)_{12} \cdot 3H_2O$) -. This uncommon mineral was formed in a limited area adjacent to the western edge of the Sacramento Stock Complex, and specimens were recovered from the Holbrook mine, first in the late 1880s, then again in the 1890s, and lastly when the Holbrook Extension of the Lavender Pit mine re-mined these areas in the very early 1970s.

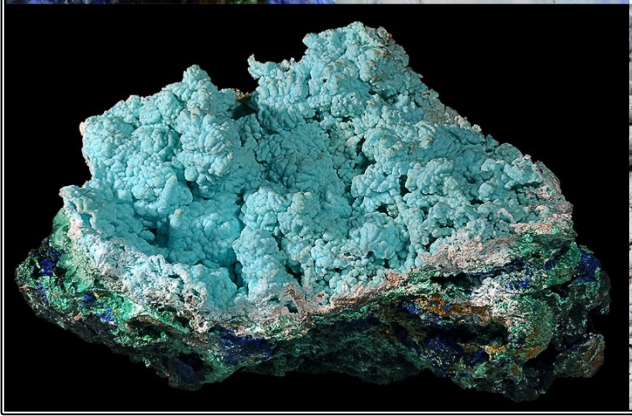
Chalcoalumite is easily and often confused with other Al minerals because of the similar appearance and the common association with azurite and malachite. This confusion is furthered by the fact that these similar-appearing aluminum minerals that are associated with azurite and malachite were mined from areas relatively close to, even within, the chalcoalumite occurrence area and at much the same time. We would speculate that fully a third of the specimens we have seen labeled as “chalcoalumite” are actually other species.



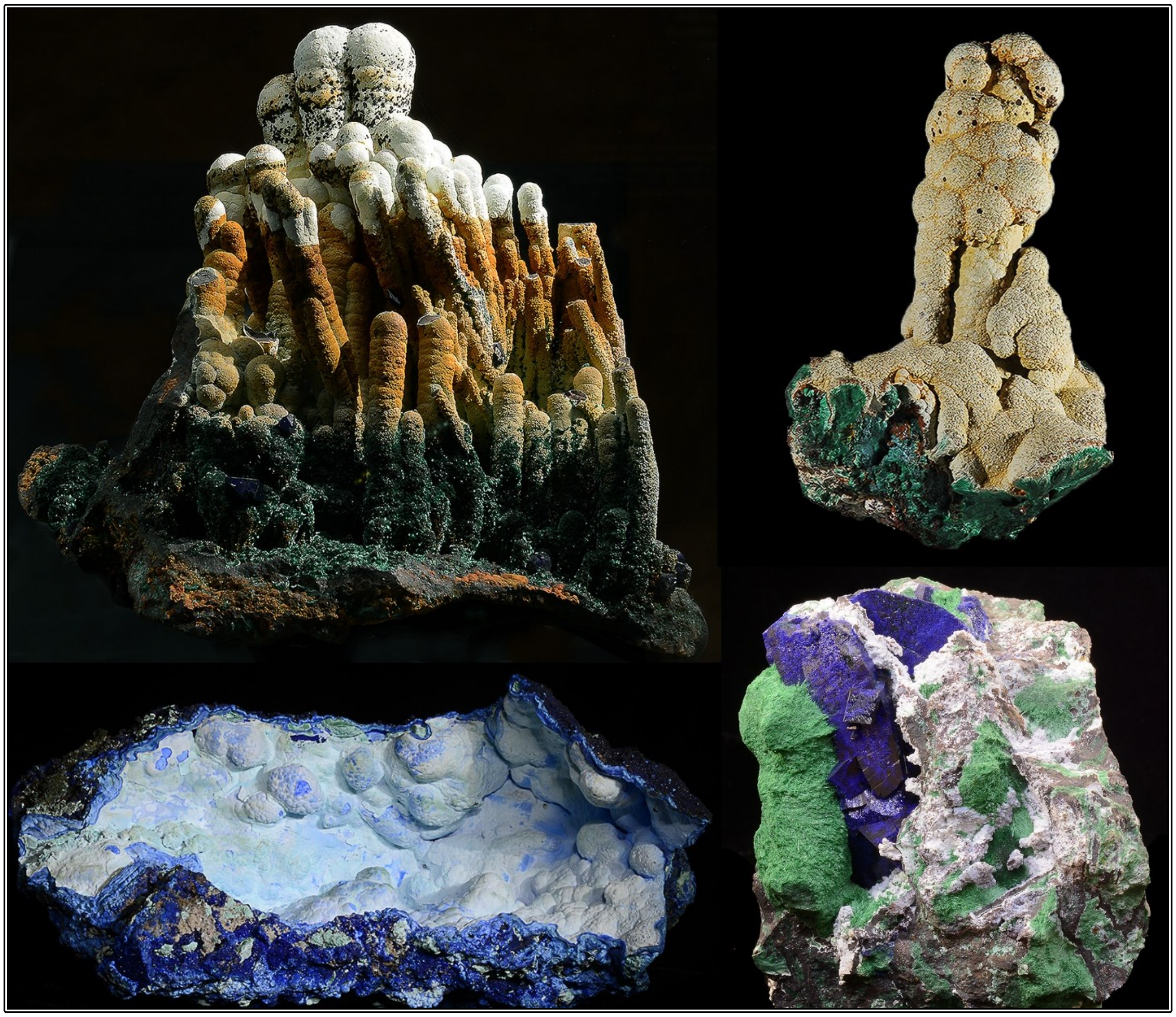
Left top: Alunite on azurite; note lack of corrosion at interface with azurite, view-4 cm, Holbrook mine, Graeme collection.

Left bottom: Chalcoalumite replacing azurite and malachite; note corrosion of the copper carbonates at the interface with the chalcoalumite, Specimen-9.2 cm, Holbrook Extension, Lavender Pit mine, Graeme collection.

Below: Azurite crystal clusters on gibbsite, view-3 cm, Holbrook mine, Graeme collection.



There are several visual clues to help distinguish chalcoalumite from other similar species. First, chalcoalumite always formed at the expense of other copper minerals, usually azurite and malachite or, less often, cuprite. Epimorphs after the earlier copper carbonates are typical, as is the presence of deeply corroded copper carbonates or cuprite underlying the crust of chalcoalumite. In contrast, the other, similar species form as a coating or crust, but with no evidence of corrosive attack by the depositing solutions. Also, similar species often have small amounts of later azurite and or malachite on the coating/crust. This is never seen with chalcoalumite.



Top left-Gibbsite on goethite with malachite and azurite, showing a distinct solution level, Czar Mine, 15.2 cm, USMNH specimen. Top right-Gibbsite as knobby crystal clusters on a malachite stalactite, Czar Mine, 11 cm, Graeme collection. Bottom left-alunite coating azurite vug, Holbrook Mine, 19 cm, Graeme collection. Bottom right- Halloysite on goethite with later azurite and malachite, 8 cm, Holbrook Extension, Lavender Pit Mine.

These aluminum minerals formed very late in the last supergene episode and totally within a small part of the western area when solutions rich in aluminum sulfate flooded a small area. There appear to be two such episodes, one of moderate pH solutions and a later, much more restricted event, but with lower pH solutions. The source of the moderate pH Al solutions probably resulted from the late-stage dissolution of the abundant kaolinite and alunite in and adjacent to the footwall of the Dividend fault.

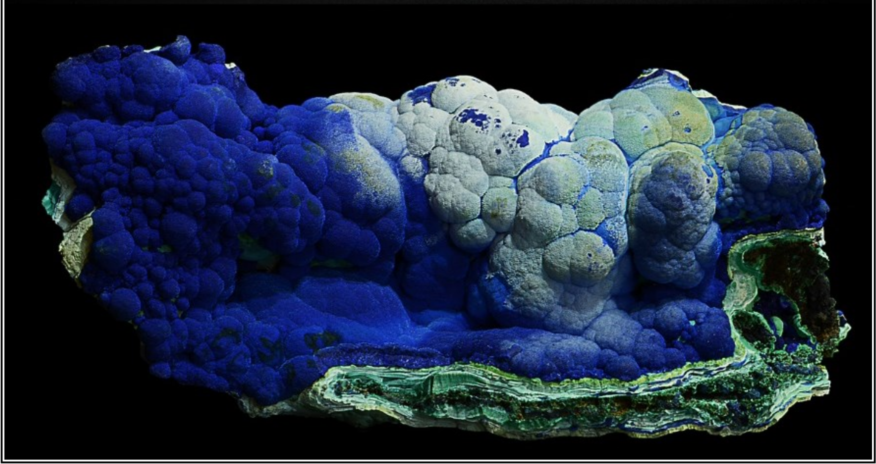
The area impacted by the earlier, moderate pH event was from just west of the Sacramento Stock Complex/ altered limestone contact in the hanging wall of the Dividend fault to about 80 meters east of the Czar shaft and south to 50 meters north of the Holbrook shaft. Vertically, it ran from just above the 200 level to almost the 400 level.

Flooded is the chosen term, inasmuch as numerous specimens demonstrate partial to complete filling of open spaces by solutions and the formation of, and the coexistence of, various Al minerals as hydrolytic products of aluminum sulfate at ambient temperatures. Examples are illustrated above.

White gibbsite along a fracture in blasted, massive goethite with minor azurite, vertical view-1.2 meters, Holbrook Extension, Lavender Pit Mine, 1970. Graeme/Larkin collection

Gibbsite, boehmite, nordstrandite, alunite, and halloysite are found as partial to complete overgrowths on goethite, azurite, and malachite as well as on other Al species. These solutions must have been of moderate pH, as the copper carbonates show no etching. This is to be expected, as Gardner (1972) shows that gibbsite will only form in a pH environment of 4.3 or greater. That these aluminum minerals may be formed under similar conditions and then may coexist in a dynamic environment was demonstrated by Sueu (1982).

Top left: white gibbsite on light blue nordstrandite which is coating azurite/goethite stalactites. Holbrook Mine, view-19.5 cm, Harvard collection.



Left bottom: Tabular, white nordstrandite crystals on azurite with malachite, Holbrook, Mine, specimen-16 cm Graeme collection.

Many such specimens with an Al mineral overgrowth were stalactitic or botryoidal in form, with vugs proving the open space aspect. In more than a few instances, local and later, minor deposition.

of malachite and azurite in subaqueous environments occurred on some Al minerals, but never on chalcoalumite, with which they are often and needlessly confused, as noted above.

The later, acidic Al-rich solutions may well have been derived through the acidic dissolution of the abundant alunite and/or kaolinite in or adjacent to the high pyrite Sacramento Stock Complex, quite late in the last supergene episode, which was ongoing at the time of discovery. The several minerals which formed during this stage of the event are all in the highly supergene altered, generally nonreactive area along the western-southwestern edge of the older porphyry.

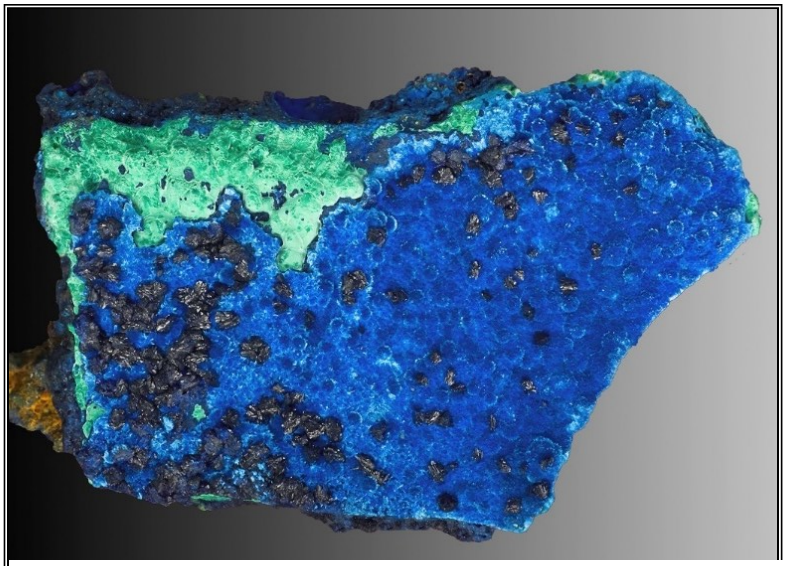
Only a small portion of the areas within the Al flooded zone was impacted by the acidic solutions. Overgrowth by the low pH Al minerals was spotty. This suggests different avenues of Al solution flow than seen in most of the typical supergene solutions. The entry area of the low pH Al solutions appeared to be almost 90^0 to the trend of the late supergene oxidizing solutions, which mostly followed the dip of the host limestones as well as structure. No doubt, the enormous masses of supergene clays already in place constrained or directed the flow of the Al solutions, as it did other solutions.

The later ingression of acidic, Al-rich solutions only impacted the eastern-most third of the area previously flooded by Al-rich solutions of moderate pH. That the area was immediately adjacent to the stock complex, a potential source of abundant acid as it contained abundant pyrite. This is a supposition at best, as even during mining and pit mapping, no physical connection was evident, but proximities were noted.

When these lower pH solutions contacted the existing copper carbonates, they reacted, forming one of several Cu/Al bearing minerals, depending on solution volume and pH, as well as the availability of copper carbonates. On the western fringes, modest amounts of Al solutions locally formed small amounts of carbonatecyanotrichite on azurite in a subaqueous environment, having robbed the necessary copper and carbonate from the underlying azurite.

Acicular, light-blue, carbonatecyanotrichite as a partial replacement of azurite on goethite with unaltered azurite and malachite. View-3.2 cm, Holbrook mine, Graeme collection.

Bright, light-blue, acicular crystals of carbonatecyanotrichite coated small areas along the edges of boxwork azurite/goethite.



Dark blue cyanotrichite, as a crust of acicular crystals to 5mm on deeply corroded malachite and azurite. Scattered, later azurite crystal clusters to 5mm are on the cyanotrichite. Holbrook Extension, Lavender Pit Mine Specimen–10.5 cm, Graeme collection.

On investigation of several specimens, the location, and manner of the deposition of carbonatecyanotrichite, strongly suggest that the source of the solutions may have been from saturated clays adjacent to the azurite and not open space solution flow or ingression. The modest amounts of goethite in the area of carbonatecyanotrichite do not have any carbonatecyanotrichite overgrowth unless previously coated by azurite suggesting the copper carbonate source controlled the deposition of carbonatecyanotrichite.

Nearby, and a bit below and with what appears to have been a somewhat greater solution volume, cyanotrichite formed as patches of 5 cm thick fibrous crystals on corroded malachite with azurite. Neither of these copper/aluminum species was abundant, and both had very minor amounts of later, subaqueously deposited azurite as 3-5 mm crystals on the new aluminum-bearing minerals.

The more acidic solutions were closer to the high-pyrite stock and entered the highly supergene altered, goethite boxwork/clay-filled environment at about 60 meters below the surface, nearly coincidental with the extent of the gossan cap, as noted during pit mapping. The occurrence of chalcoalumite at Bisbee was restricted to an area of fewer than 70 meters horizontally and ±50 meters vertically, following the trend of the ores.

Any and all copper carbonates near the west end of the stock and within the flow area of the solutions were attacked by those solutions and replaced to varying degrees by chalcoalumite. Chalcoalumite generally occurred as faithful, but often friable, casts of malachite and epimorphs of azurite.

The closer to the stock, the higher the degree of replacement of the copper carbonates occurred. In some cases, the replacement was complete, with even the normally inert goethite exhibiting signs of acid corrosion. This was what the very first chalcoalumite was like when found in about 1888 and mined from a few small orebodies for several years. It was not recognized as something new or different, as it so closely resembled chrysocolla and other blue-green mineral crusts on malachite and azurite, which were common. In 1925, Larsen and Vassar described chalcoalumite and correctly predicted that much more would be found on examination.


Chalcoalumite as a complete replacement of malachite and azurite on corroded goethite. One area hosts tiny crystals. This specimen was sold by noted mineral dealer A. E. Foote in 1890 or before and still carries his "chrysocolla" label. Holbrook mine, specimen-7.8 cm, Graeme collection.

Later, mining during the first decade of the 20th century, produced much more chalcoalumite, albeit still unrecognized. It differed in the degree of replacement. The total replacement of the copper carbonates was seen, reflecting its proximity to the stock. A bit further from the stock and lower, the replacement of the carbonates was substantially less complete. While the surface still faithfully reflected the form of the original malachite/azurite, the material just underneath is usually a porous crust from a few millimeters to nearly a centimeter in thickness with substantial azurite and malachite underneath.

Chalcoalumite as a partial replacement crust of malachite and azurite, specimen-12 cm, Holbrook Extension, Lavender Pit Mine, Graeme collection.

The extension of the Lavender Pit to the west once again entered the limited part of the deposit that hosted chalcoalumite. This time we knew what we were looking at and sought a better understanding of the "why, where, and when" of this odd mineral. Its light color stood in stark contrast to the red-brown of the hosting oxide/clays, aiding greatly in collecting, but the staining of the soft oxide/clays made cleaning a frustrating task. And too, the very friable nature of the chalcoalumite made collecting damage-free specimens nearly impossible. Nevertheless,

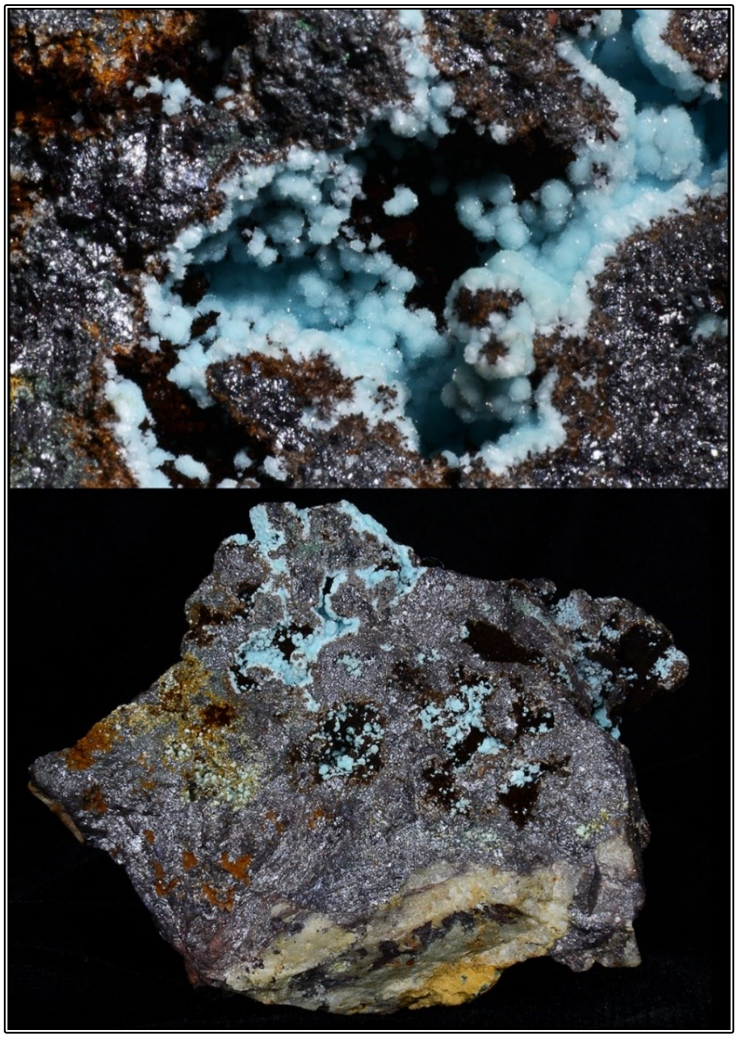
Chalcoalumite as an epimorph after azurite and as scattered spherical clusters of tiny crystals, with cuprite on slightly corroded goethite. View-3 cm, Holbrook Extension, Lavender Pit mine, ASDM collection.

When we found this specimen in April 1970, the epimorph form was filled with pulverant, iron-stained malachite, which washed away. The specimen was gifted to George Bideaux soon after it was collected.

hundreds of specimens were recovered while mining followed the trace of this mineralizing event from level to level over several years.

The incredibly richly mineralized intrusion breccia along the south and west sides of the stock was also highly silicified and relatively impermeable to supergene fluids. However, small areas of the western portion had been altered to massive cuprite in the form of huge masses exceeding several tens of tons. Adjacent to the cuprite were areas of incredibly hard goethite with numerous boxwork voids with abundant malachite, azurite as well as cuprite as 3 to 5 mm crystals.

The low pH, high Al solutions attacked the margins of both of these types of supergene mineralization. In the cuprite, small, preexisting, irregularly shaped voids were depositional sites for 0.2 mm chalcoalumite crystals in spherical clusters with cuprite providing the copper. The hard goethite had lesser amounts of similar chalcoalumite crystal clusters and epimorphs of azurite crystals.



Left, Two views of the same specimen, with chalcoalumite in cuprite as 0.5-1.0 mm spherical clusters of tiny crystals, specimen-9 cm, Holbrook Extension, Lavender Pit Mine, Graeme collection.

The discovery of these crystals by local collector, Al Voirin, allowed Sid Williams and Basha Khin (1971) to complete the work of Larsen and Vassar (1925) by defining the crystal form.

In reality, tiny crystals of chalcoalumite did occur on some of the early specimens but may not have been available for review or too small to be useful for the 1925 study.

What Hawthorne and Cooper (2013) did was to refine the crystal structure by determining the positions of the atoms in the unit cell to three decimal places.

Continued mining exposed more of the areas which had experienced at least some exposure to the low pH solutions. Areas that did not contain reactive minerals, developed patches of thin, almost hairlike white crystals that had effloresced from the soft clays as they dried. Tasting this efflorescence suggested it was an Al sulfate, perhaps alunogen, hydrobasaluminite, or felsőbányaite. The latter two were found in some quantity a bit deeper. (We have long used taste for rough element detection of soluble minerals and have found it useful for Fe, Cu, Zn, Mn, and Al).

Altered limestones and the siliceous nature of the intrusion breccia stopped the progression of the Al-rich solutions near what became the Holbrook shaft site. Massive alunite/gibbsite/halloysite had been deposited in modest amounts by moderate pH solutions. The substantially lesser volumes of the low pH, Al-rich solution deposited hydrobasaluminite, which quickly altered to felsőbányaite on exposure due to mining. As a point of interest, both hydrobasaluminite and felsőbányaite have been recognized elsewhere at Bisbee as post-mining occurrences.

Chalcoalumite was never found in any other part of the mineral deposit. Several of the other Al minerals were found elsewhere. Alunite was common and abundant to the point it was used to line the smelter furnaces (Douglas, 1900). Both gibbsite and halloysite were common supergene minerals in several other areas of the deposit.

A FEW NOTES ON THE DEPOSITION OF AZURITE AND MALACHITE:

Over the years, we have noted several of the depositional features that control or influence the deposition of azurite and malachite. Our observations bring nothing new to science, but if noted elsewhere in the scientific literature, they are obscure and hard to find. The following remarks are apart from the Eh/pH aspects discussed below and relate to field observations as well as laboratory investigations.

We have chosen to discuss only azurite and malachite, as these are undoubtedly the most important of the species for which Bisbee is noted. And too, the huge number of specimens available in collections around the world, which are available for study, aid greatly in confirming concepts. Equally important is the fact that they were the most common copper minerals we found while doing our field studies, allowing close looks at the environments. The frequent shifting from the deposition of one carbonate to the other, as well as the change in depositional environments from subaerial ↔ subaqueous, can be tracked at the point of deposition.

From field observations, malachite almost always forms first, often in minimal amounts initially. This appears to be a more-or-less site preparatory in nature, liberating CO_2, which will build up in the depositional environment, allowing azurite to form if the pH is below 8 and the CO_3 activity is low. The malachite/azurite transition is very sensitive to small chemical changes in the environment: equilibrium is reached at $PCO_2 = 10^{-3.45}$ atm., i.e., close to normal values, whereas the precipitation of both minerals from cupric-ion-bearing solutions takes place at pH values between 6 and 8, depending on CO_2 partial pressures. It is shown that the stability relations of these minerals can be better explained in terms of activities of the carbonate and bicarbonate ions.

WHICH COMES FIRST – AZURITE OR MALACHITE?

Left: Malachite as the first copper carbonate deposited on malachite/goethite boxwork forms. It is from a subaqueous environment, followed by azurite, also deposited in a subaqueous environment. Czar Mine, view-7 cm, Graeme collection.

The goethite boxwork suggests that the supergene activity was well advanced, while the nature of the copper carbonates indicate deposition by exotic solutions, having experienced some transport.

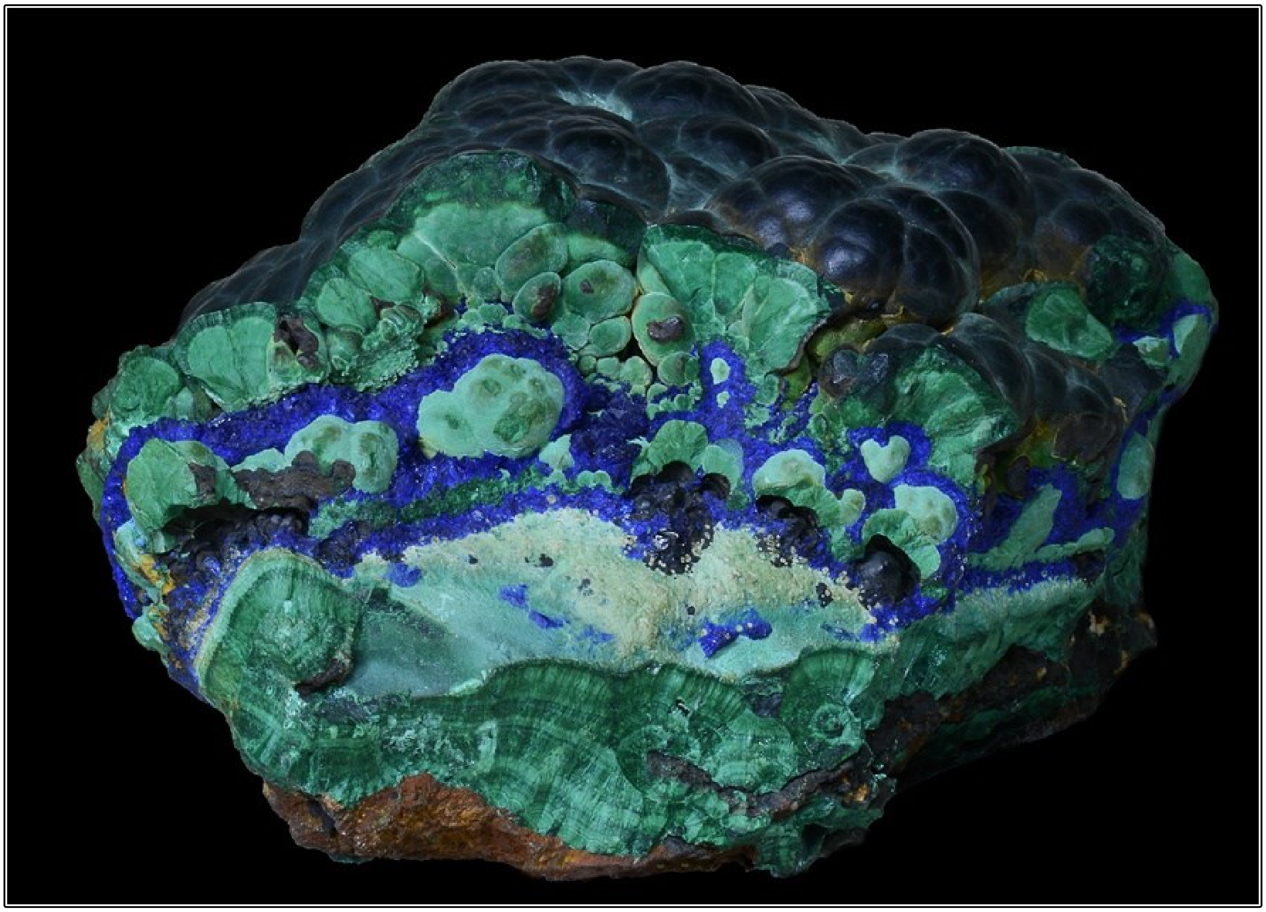
This is more than a riddle, as understanding the environment through the varying cycles of the multiple supergene episodes aids in the understanding of what is seen in a specimen. This, in turn, helps to understand the supergene process at the source of the sample. Inasmuch as we have field collected many of the specimens studied, we can put this information into an overall context.

Reviewing several hundred azurite/malachite and azurite with malachite specimens with this in mind, we found that in the vast majority of cases, malachite is deposited first, albeit sometimes in minor amounts.

This holds true for both subaerial and subaqueous depositional environments. The copper-containing sulfides are much slower to be affected by supergene activity than pyrite. As previously noted, the acid generated by the decomposition of pyrite does much to accelerate the breakdown of copper sulfide minerals. As discussed previously, the formation of siderite can and often does create a very high CO_2 environment. This should favor the deposition of azurite. Why does the early formation of malachite seem so prevalent? In no small part, the continued exposure of siderite to low pH solutions, something quite common, will reduce the CO_2 concentrations and increases the available O_2 while forming goethite, thus favoring malachite.

And too, Vink (1986) shows that this is a function of the activities of the carbonate ion in solution rather than the partial pressure of carbon dioxide in the atmosphere, as pH is now the driver. This suggests an excess of buffering capacity remaining. Given the limestone host rocks, this makes sense. The continued acid generation does consume the CO_3^{2-} and allows the formation of azurite. The amount of malachite formed before azurite or during transition periods between malachite and azurite formation gives a relative indication of the duration of excess CO_3^{2-}.

In cases where little pyrite was available to buffer the surrounding limestone and form siderite while generating little CO_2, it makes intuitive sense that malachite would form first, as the supergene process is in its early stages. It is likely that the buffering of acidic, cupric solutions has not consumed the available CO_3^{2-} or advanced enough to have generated sufficient CO_2 to push the system toward azurite formation. Vink (1986) stated, "*The same is possible for pH, given that the earlier solutions would find an excess in buffering capacity in the newly contacted limestone, thereby raising the pH outside the azurite formation window. Continued solution ingress would create more CO_2, while simultaneously reducing the buffering capacity, allowing* the *pH to lower.*"



An example of Malachite as a layer of compact, banded, subaerial material grading into similar appearing subaqueous malachite, topped by a thin layer of gibbsite. Crystalline, subaqueous azurite was deposited on the gibbsite, followed by subaqueous malachite, then another layer of subaqueous azurite, with a thick layer of subaqueous malachite and, finally, a thin veneer of hard, compact subaerial malachite.

The hard goethite/hematite base indicated deposition by largely indigenous solutions and that the supergene process was somewhat advanced when copper carbonate deposition began. The transition to a subaqueous environment reflects a possible source change to exotic fluids, which persist, while the deposition of gibbsite suggests a pH of 6.5-7 (McHardy and Thompson, 1971).

Holbrook Extension, Lavender Pit Mine, Specimen-20 cm wide, Graeme collection

As the transition of malachite ↔ azurite is quite sensitive to the partial pressure of CO_2, pH, and the activities of CO_3^{2-} (Vink, 1986), the change from one to the other can give insight into the prevailing conditions and their fluctuations. This aids in recognizing different supergene events as well as the changing solution conditions over time. Even very minute changes in solution chemistry and in the environment may influence the formation and stabilities of azurite and malachite.

Vink (1986) noted that: *"…the precipitation of azurite and malachite from cupric-ion-bearing solutions is equally sensitive: azurite will be precipitated at pH values between approximately 6 and 7, at* pCO_2 *values >* $10^{-3.45}$ *atm., and malachite at pH values between approximately 7 and 8, at* pCO_2 *values <* $10^{-3.45}$ *atm., the turning point being at pH = 6.95 with a corresponding* $p(CO_2) = 10^{-3.45}$ *atm."*

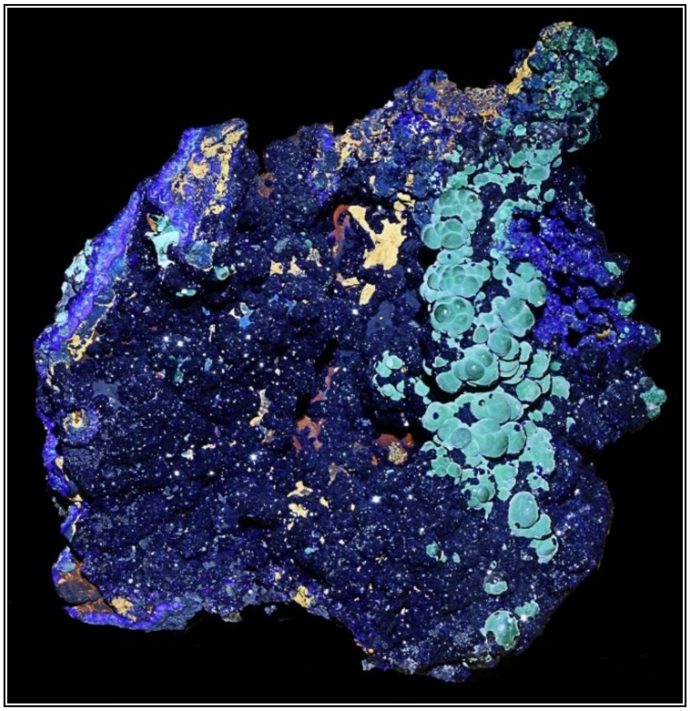
With this understanding, general assumptions can be made of the chemical-atmospheric environments to track their fluctuations better. An interesting aside from this review is that most Bisbee malachite and azurite specimens are partial to complete azurite overgrowths of malachite. Given the relatively wide range of Eh-pH where malachite is stable, the later deposition of azurite rarely seems to affect the malachite. However, where malachite has been deposited on azurite, it is common, but not universal, to see some dissolution of the azurite. A review of the Eh-pH diagram of Vink (1986) shows a substantial overlap of the malachite phase over the azurite phase; thus, the reason some malachite deposition does not affect azurite, while another may cause dissolution.

AZURITE:

Azurite has two principal modes of deposition. These are subaerial and subaqueous, the latter usually with exotic fluids that have migrated at least some distance from the supergene oxidized sulfide source. The rose/nodule formation, which was discussed previously, is essentially subaqueous.

DEPOSITION:

Subaerial azurite is largely deposited as a gel. The band thickness varies greatly, as does the hue, which is normal. The presence of Liesegang rings only in the subaerial deposited material further supports this observation. We have seen post-mining azurite forming in long-abandoned workings where it was up to several centimeters thick and still gelatinous. The high surface tension of the gelatinous material gave the reniform features so commonly seen.

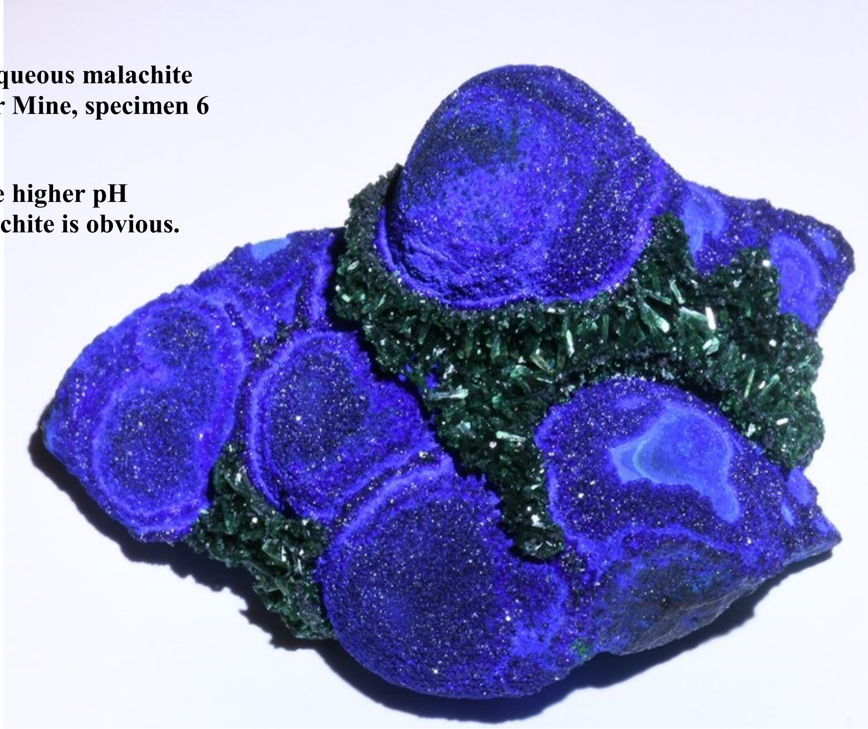


A pair of azurite and malachite specimens showing that the malachite remains totally untouched by the subsequent azurite deposition.

Left subaqueous azurite on malachite Czar Mine, specimen-10.5 cm, Graeme collection. Right, Azurite as light blue subaerial material largely overgrown by dark, subaqueous, crystalline material. Czar Mine, View-17 cm, Harvard Collection.

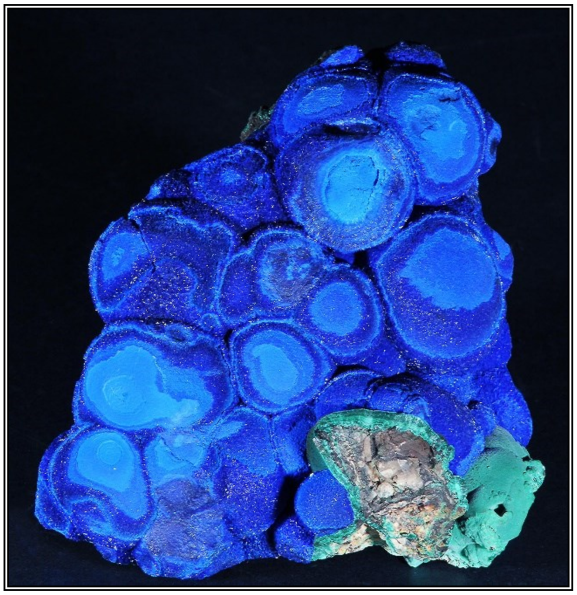
Right: Uncommonly, stout subaqueous malachite crystals to 4 mm on azurite. Czar Mine, specimen 6 cm.

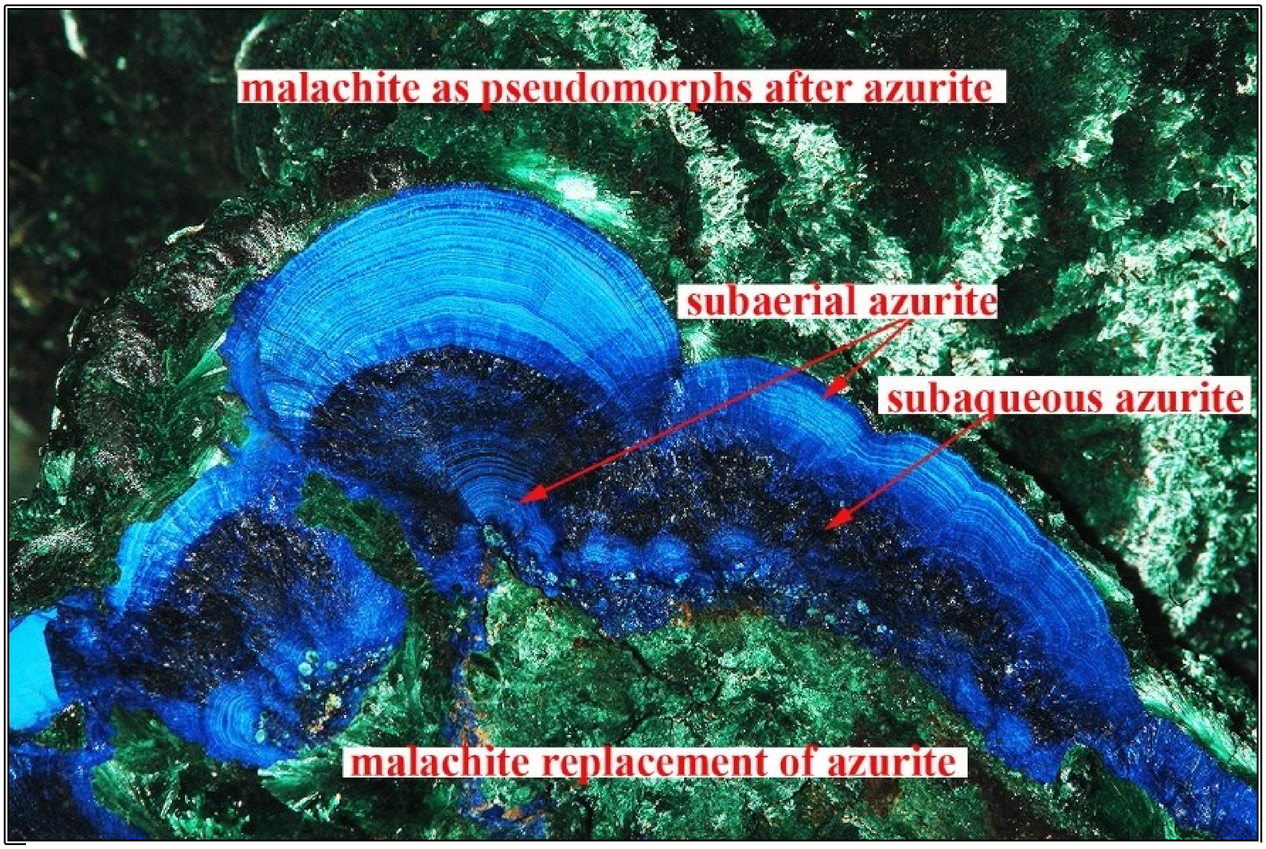
Corrosion of the azurite from the higher pH solutions that deposited the malachite is obvious. Graeme collection.



Right: Deeply corroded azurite, largely of subaerial origin followed by a minor subaqueous deposition event before high pH solutions began attacking the azurite. All corrosion in at the same level when the specimen is rotated to a point where the corroded areas are oriented downward. Modest malachite is coating a chert fragment from the replaced Escabrosa limestone. Holbrook Mine, specimen 9.8 cm. Graeme collection.

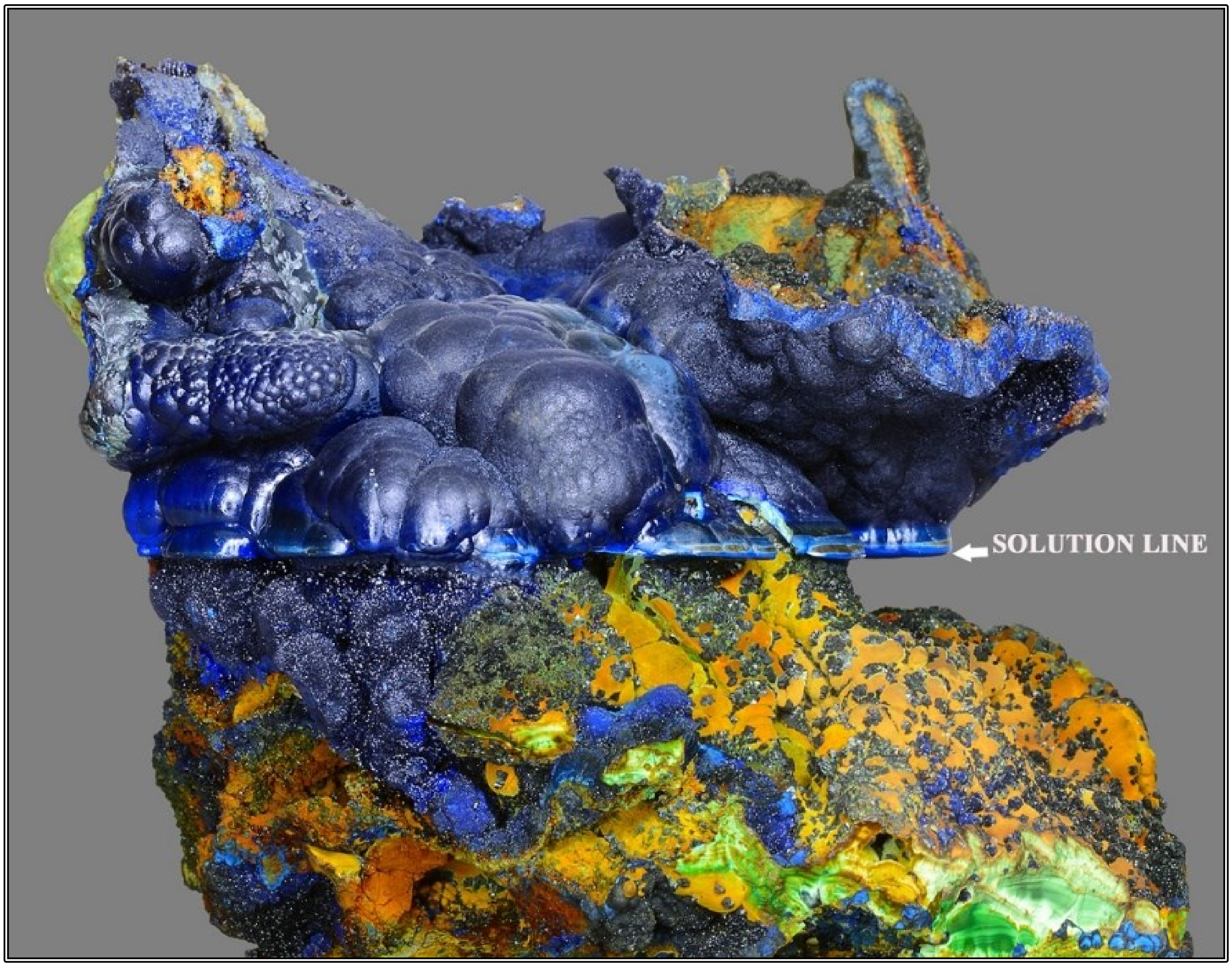
Other similar specimens we have seen reflect the same feature showing the corrosive solutions in the void raised in level, but did not fill the opening.





Classic banded azurite with malachite above and below, both of which have replaced azurite. The azurite reflects three depositional phases, with the first in a subaerial event, followed by a subaqueous episode, then subaerial deposition. The capping malachite is a coat of five mm pseudomorphs of malachite after azurite, reflecting a subaqueous period.

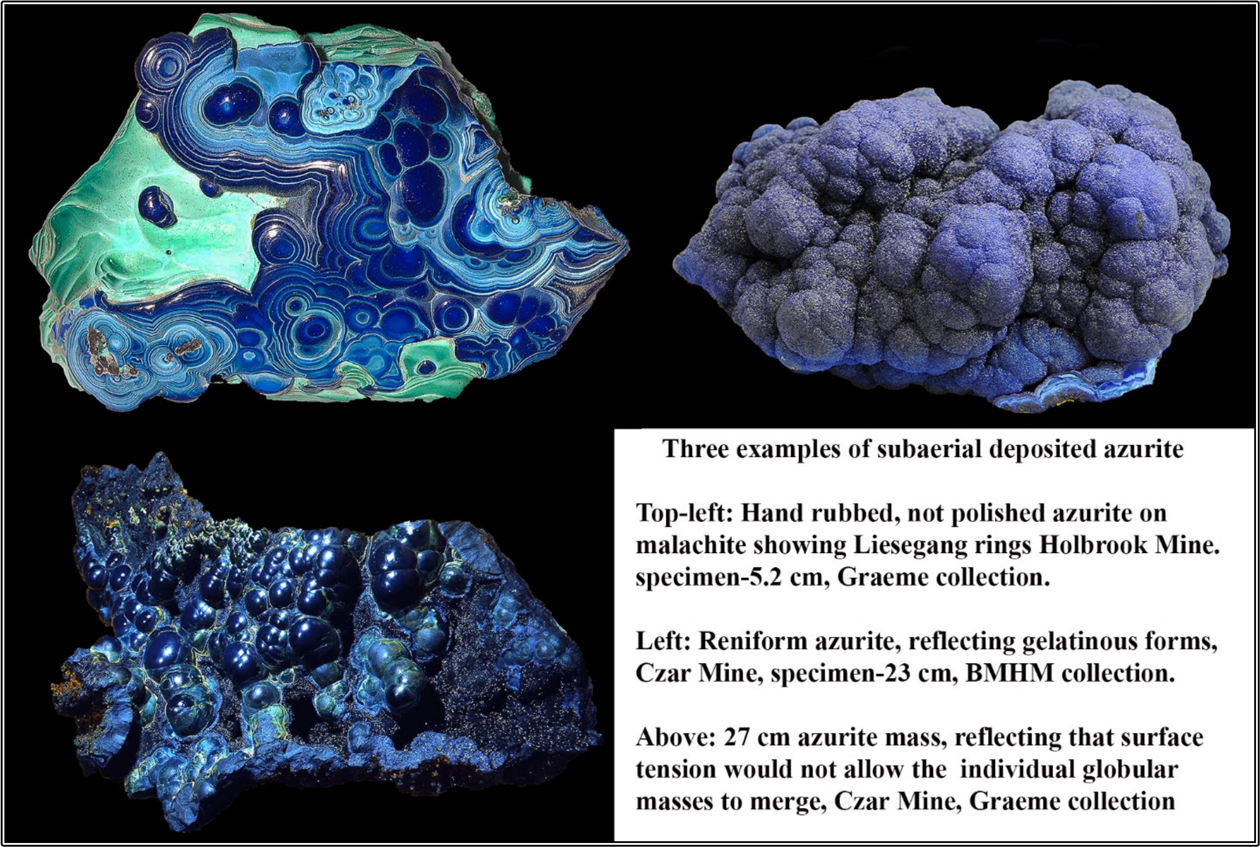
It would appear that the alteration of the pseudomorph crystalline layer protected the banded material from alteration, but why did the alteration stop at the banded interface? View-6 cm, Holbrook Mine, BMHM collection. Photo Graeme/Larkin collection



An extraordinary, 18 cm wide specimen that clearly demonstrates the air/solution interface as related to azurite deposition.

The paragenetic sequence is difficult to see. It is, first, a skin of subaerial malachite then minor subaerial azurite deposition followed by substantial subaerial malachite, and very minor subaqueous goethite, more as a stain than a coating, followed by tiny cuprite, as clusters of octahedral crystals, reflecting the lower pH and lack of CO_2, and lastly, with a lower solution level, azurite as both subaerial-non-crystalline and subaqueous crystalline, drusy to the left in this case. Surface tension of the gel would have created the shelf at the air/solution interface. Czar Mine, Graeme collection.

Right: A closeup of the small slot broken out of the azurite shelf where at least two previous solution levels were evident. The steep incline suggests an 8 mm lowering of solutions. View 2.2 cm

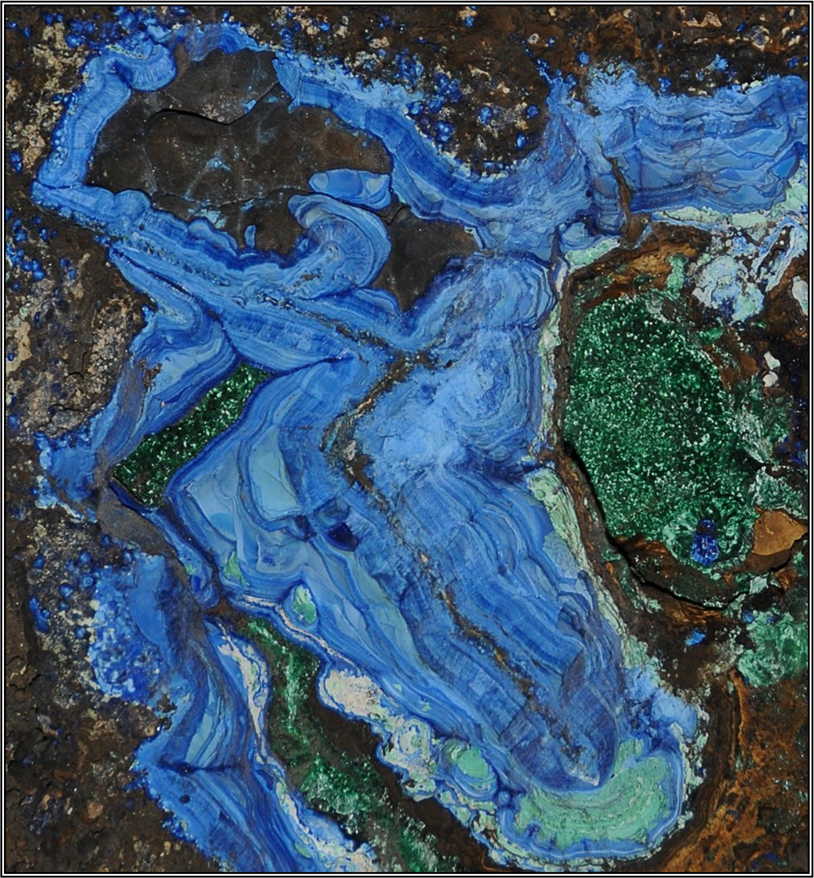


Three examples of subaerial deposited azurite

Top-left: Hand rubbed, not polished azurite on malachite showing Liesegang rings Holbrook Mine. specimen-5.2 cm, Graeme collection.

Left: Reniform azurite, reflecting gelatinous forms, Czar Mine, specimen-23 cm, BMHM collection.

Above: 27 cm azurite mass, reflecting that surface tension would not allow the individual globular masses to merge, Czar Mine, Graeme collection



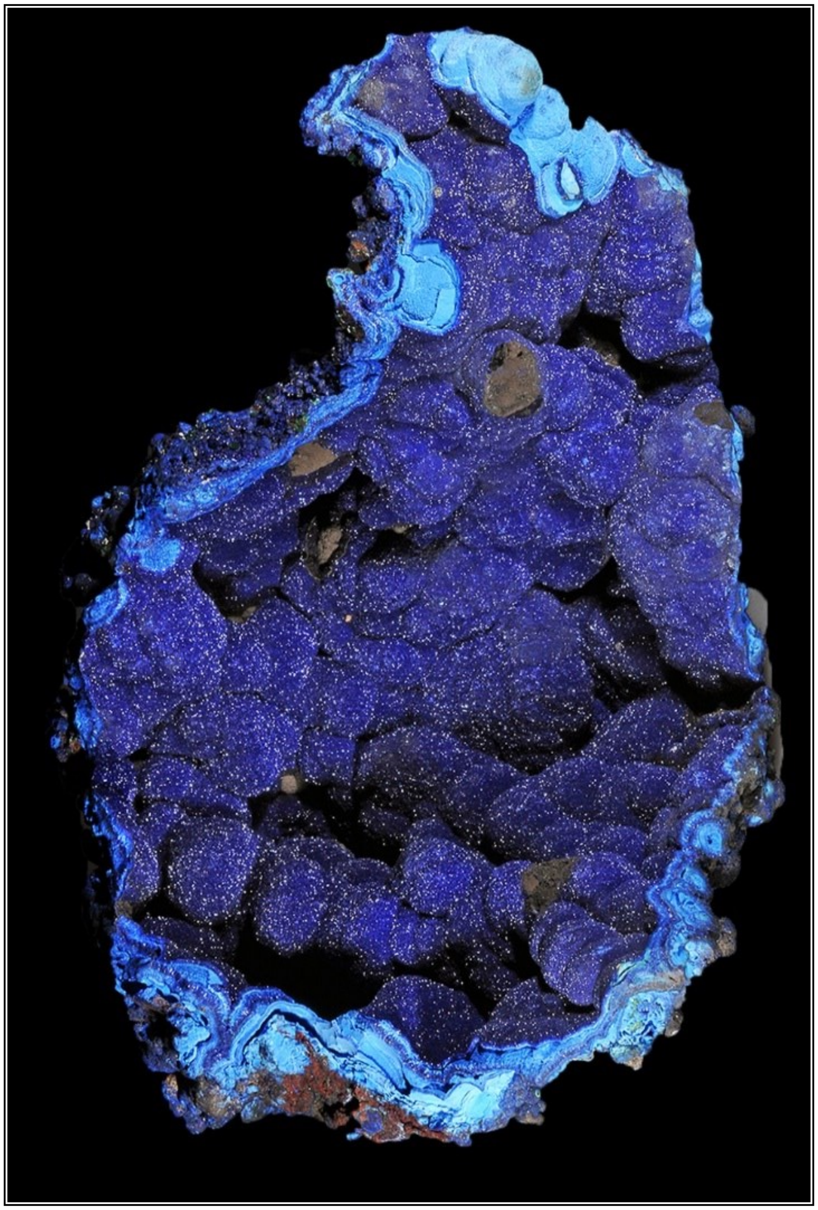
Left: Subaerial deposited azurite has completely lined this void. Other voids are nearly completely filled by this azurite. Void lining is a feature common to both azurite and malachite under subaerial conditions.

This is a closeup of a section of the large block in the AMNH. 200 level, Czar Mine, view-35 cm.

The following information is based on our field observations and the conclusions derived from these. No field measurements of any factors were ever taken, and, in some cases, as much as 40 years had elapsed between visits. Some have photographs from the 1950s and 1960 as well as post-2000 photographs, recording the changes, but they are few.

The solutions that deposit azurite and malachite in subaerial environments appear not to have traveled very far from the point of origin – oxidizing sulfides solutions were buffered by the hosting limestone. This includes the in-situ depositional environment. They tend to be slightly more viscous than normal groundwater. Some markedly so and are even mucous-like to the touch. In many regards, they are quite similar in behavior to the common iron hydroxide depositing solutions, seen so often in oxidizing sulfide zones.

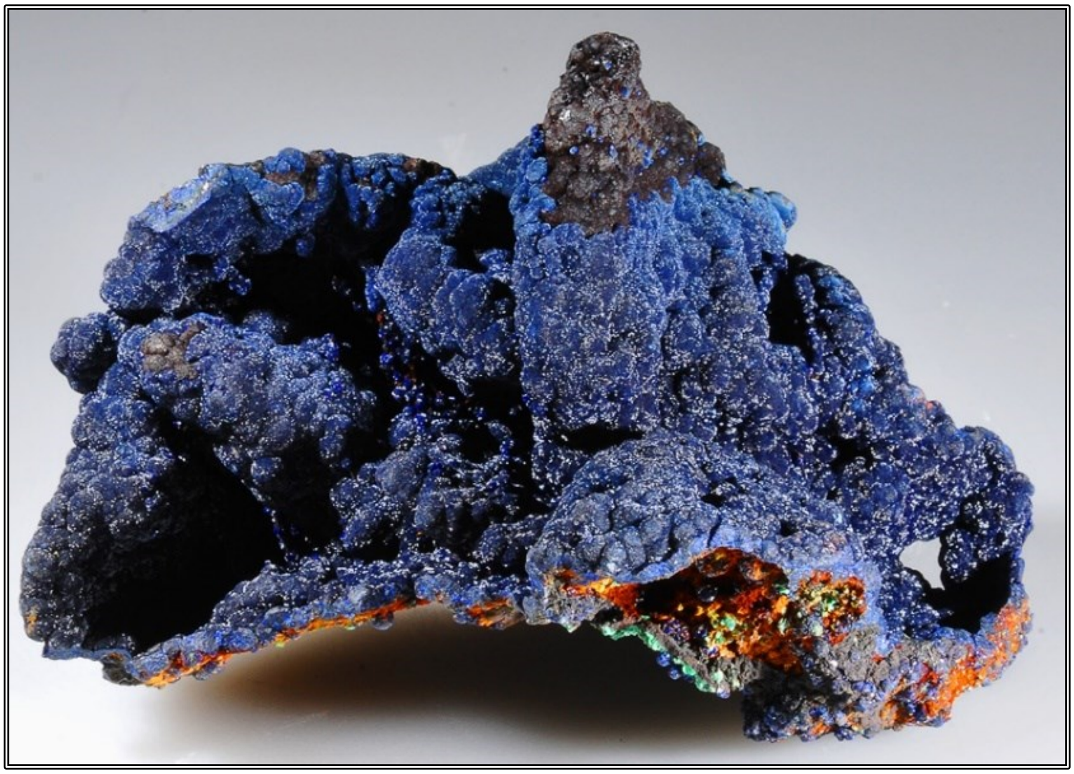
When these solutions enter an air-filled void, they tend to spread out and ultimately line much of what is below the level of the entry point. It is quite common to have an azurite or malachite specimen that is the whole of the deposited copper carbonate within a void, both as a partial and complete lining.



Left: An azurite-lined vug from a goethite/Mn oxide mixture. Note the near-completed lining, except in a few spots where highpoints of the underlying Mn oxide reacted with the surface tension of the azurite gel, not allowing it to cover the material, something often seen in subaerial deposited copper carbonates at Bisbee

Holbrook Mine, Specimen 15 cm, Graeme collection.

Normal, $CaCO_3$-charged groundwater will typically follow a preferred path, depositing calcite along this pathway. With groundwater, the remainder of the void will only have calcite deposited if the space is filled. Azurite and malachite tend to coat more of the void due to the higher viscosity. Along the upper edges, it is common to see a bit of an uneven, upward creep in deposition due to the high surface tension and capillary action. This characteristic is visible in the illustration below.



A goethite/Mn oxide vug, partially lined with subaqueous azurite. Note the near-completed lining and the top of the azurite, where surface tension together with capillary action, caused the deposition unevenly on the Mn/goethite above the apparent solution level.

Holbrook Mine, Specimen 15 cm, Graeme collection.

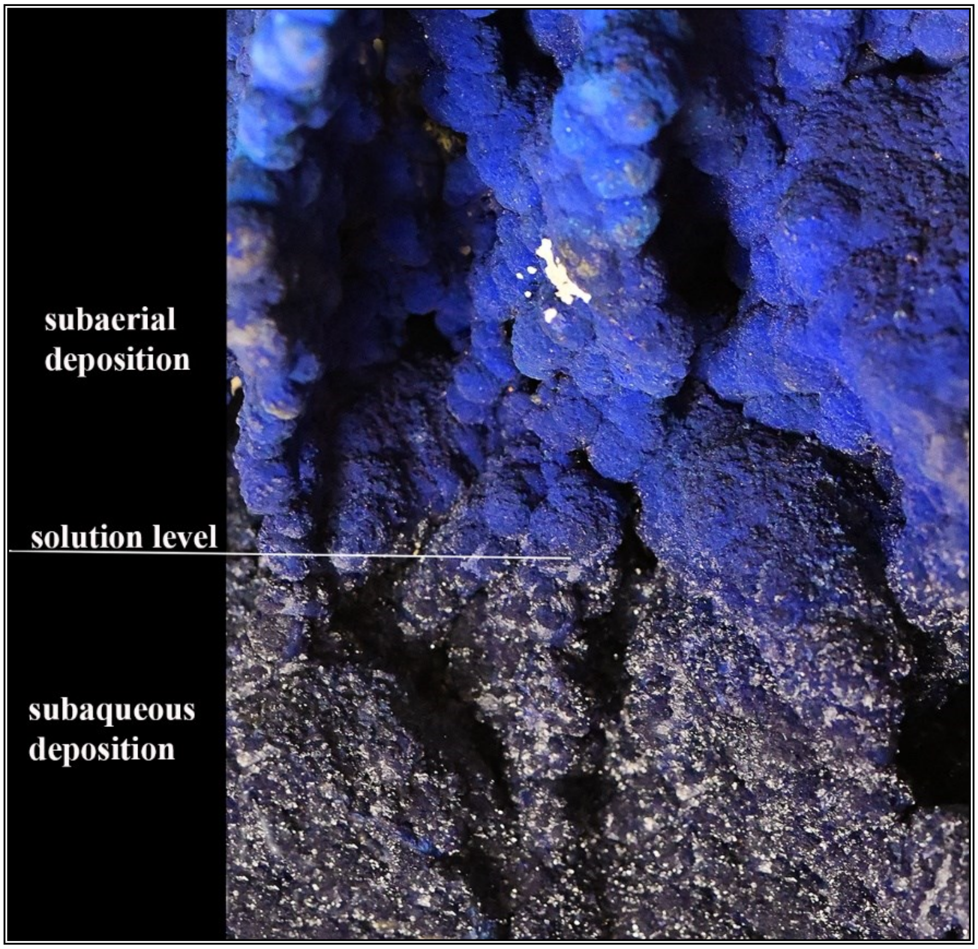
The depositional environments fluctuated due to geologic uplift, tilting, and changes in solution chemistry, variations in climate, and groundwater levels. Any or all of these events can be seen reviewing various specimens. Thus, it is common to see specimens that reflect more than one depositional episode/environment.

Azurite deposition in a subaerial environment is massive and often banded, while subaqueous is typically crystalline. Fluctuating environments often imprint one on top of the other. It is quite common to see multiple fluctuations in a single specimen. The specimen shown below reflects a single period of partial submersion on subaerial material.

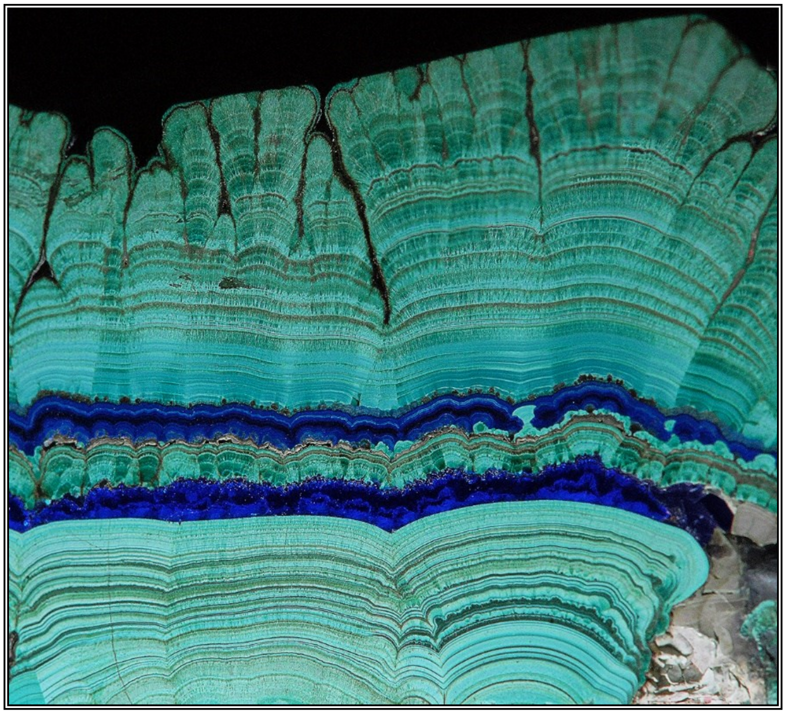
Right: Subaerial deposited azurite above subaqueous deposited azurite. The white material is candle wax from a miner's candle at the time of collection - prior to 1913.

Holbrook Mine, Vertical view-5cm,

U of A collection.



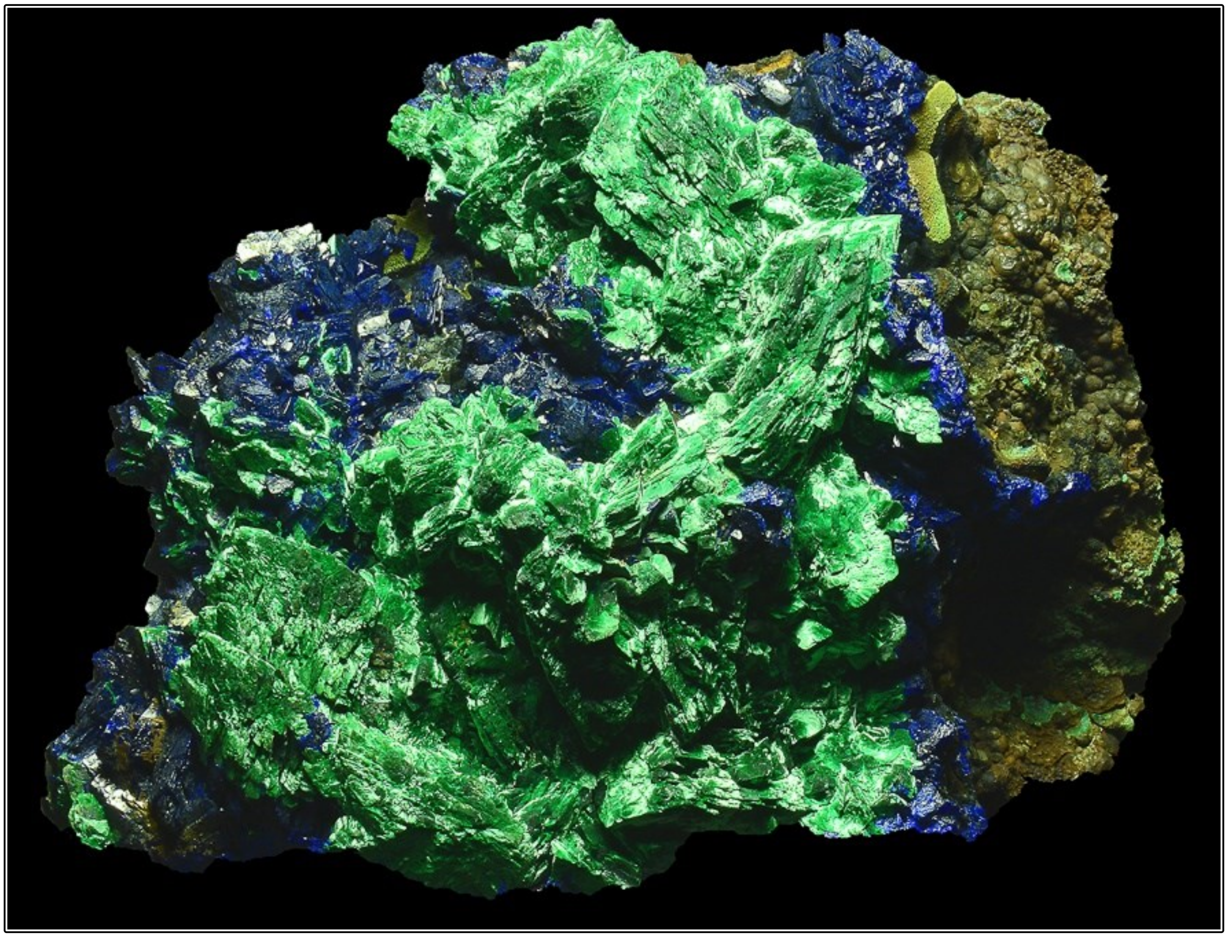
Right: An example of multiple, fluctuating, environments; Subaerially deposited malachite at the bottom, coated by subaqueous azurite, that is covered by a thin layer of a Mn oxide, in turn covered by subaqueous malachite, again a paint-thin layer of Mn oxide, then subaerial azurite followed by subaerial malachite and, lastly, a thick deposit of subaqueous malachite as closely packed acicular crystals, Horizontal view-4.8 cm, Holbrook Mine, Graeme collection.



REPLACEMENT BY MALACHITE:

The replacement of azurite by malachite was a common, reoccurring feature of the various supergene episodes. Fluctuations of p(CO_2) gave rise to replacements, and multiply banded copper carbonates will form if not all of the pre-existing material is reacted away under changing solution conditions. The new material crystallizing on the surface may protect what is present underneath, as is so commonly seen with malachite over azurite.

Other species covering azurite have been recognized as protecting it from alteration. Soft manganese oxides were particularly abundant in supergene altered Martin limestone and often deposited with the copper carbonates as a crust to a thin, paint-like layer.
Malachite, as pseudomorphs after azurite, is extremely abundant throughout all of the supergene altered orebodies. Excepting roses, we have seen every one of the many varied azurite crystal forms recognized at Bisbee as a malachite pseudomorph, though more often as a second-generation overgrowth, as will be detailed later. Also, we have malachite pseudomorphs after azurite forms that we have not seen as azurite crystals.



Subaqueous deposited azurite with malachite pseudomorphs after azurite of the same morphology. When found, the remaining azurite was covered by soft, claylike Mn oxides, which were easily removed by washing. It would appear that the Mn oxide protected the covered azurite from alteration. Holbrook Mine specimen-12 cm, Graeme collection.

There are two forms we have not confirmed as malachite replacements. The replacement of banded, subaerially deposited azurite that has been replaced by malachite is undoubtedly present, indeed perhaps abundant. However, we have not seen something that is unquestionably such a replacement. The near-identical forms of the two probably mask the change.

The second azurite morphology not seen as malachite pseudomorphs is very late-stage azurite in pseudo-rhombohedral forms to two centimeters that was deposited in boxwork voids within a dense quartz/hematite mixture near the Sacramento stock.

These may well be so young as to never have experienced the necessary environment shift to affect the alteration. Malachite pseudomorphs after the classic rose forms are known in several turn of the 20th-century collections, but in all cases, the provenance is uncertain, and we question the source.

As with most azurite/malachite occurrences worldwide, specimens of azurite in the process of altering to malachite are found in Bisbee but not in the quantity or manner as seen elsewhere. Very few Bisbee locations have produced specimens that capture the alteration in the process in progress. Yet, there are numerous Bisbee localities that show this alteration was carried to completeness. It is common to see several such events interspersed by deposition and subsequent alteration.

For specimens demonstrating partial alteration, the most prolific area was the 800 level of the Cole Mine. Here rose-like forms were often partially altered. Masses of somewhat altered azurite were the base of 1-2 cm, completely altered tabular crystals. These both lacked the deep corrosive appearance of alteration as often seen elsewhere. Nor do they show what Palache and Lewis (1927) characterized much of the Tsumeb, Namibia azurite alteration to malachite as "*The malachite fibers radiate from one important center on the front pinacoid, and many interfering centers….*" This feature is extremely uncommon at Bisbee, with but a few examples known where the alteration was complete but still reflect radiating features as noted at Tsumeb.

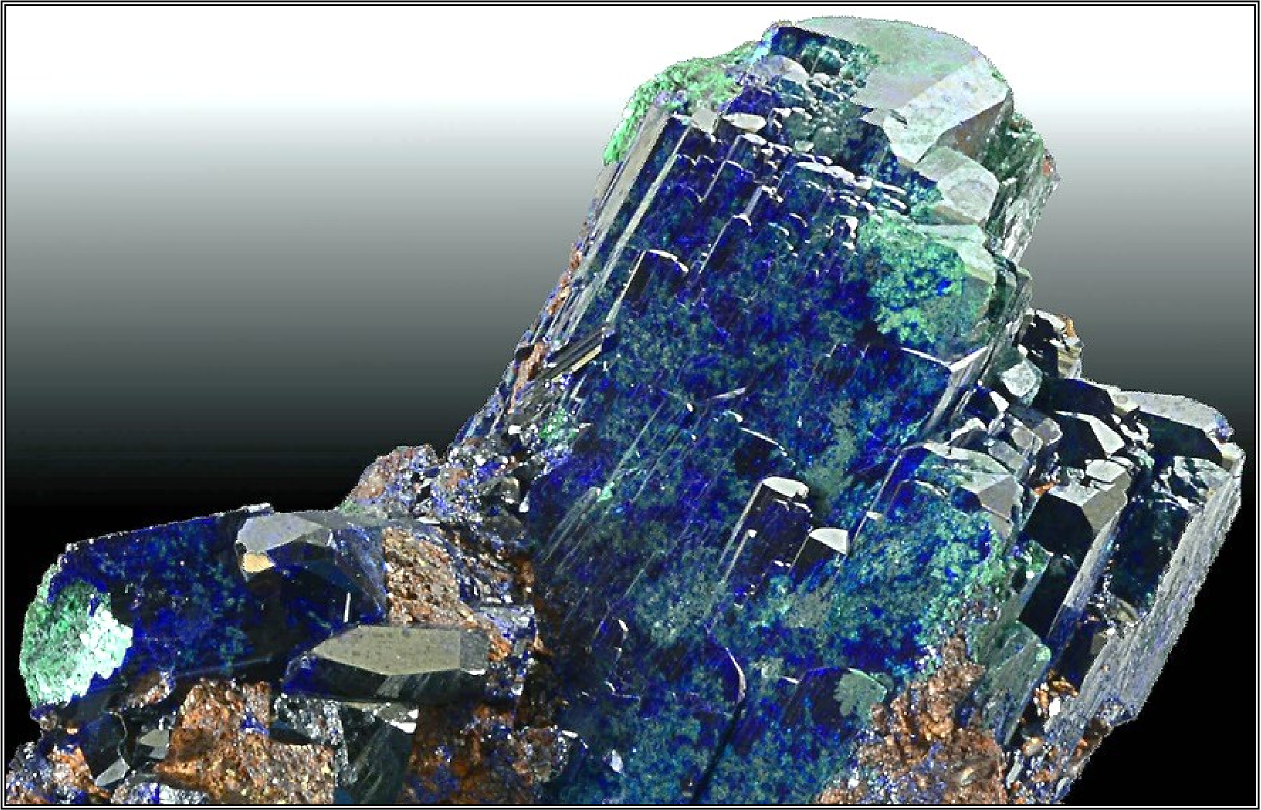
SECOND-GENERATION OVERGROWTHS:

No doubt that much confusion concerning specimens seemingly altering to malachite results from a near-universal feature at Bisbee for large azurite crystals, those > 1 cm. All are second-generation overgrowth on a malachite pseudomorph after azurite. These are almost always confused with in-process alteration. A close look at the interface between the azurite and malachite will show crystal faces and not corrosion effects. Just a few examples from the 200 level of the Czar mine are not overgrowths. The wonderful azurite roses from the Czar and Holbrook mines are an exception as well. The reasons for this have been previously explained.

A fine illustration of this phenomenon is the specimen pictured below. It came from the easternmost and deepest azurite occurrence in the district. The wonderful stope produced numerous, large second-generation azurite overgrowths in the late 1930s. Interestingly, different parts of the orebody produced different crystal forms, all altered to malachite.

However, only this crystal form had a second-generation of azurite deposited on the pseudomorphs. Some areas showed no secondary growth, while others were covered by subaqueous malachite as a secondary overgrowth. In both instances, they were completely embedded in dense, hematitic clay, but the crystals with a second-generation of azurite were in open voids.

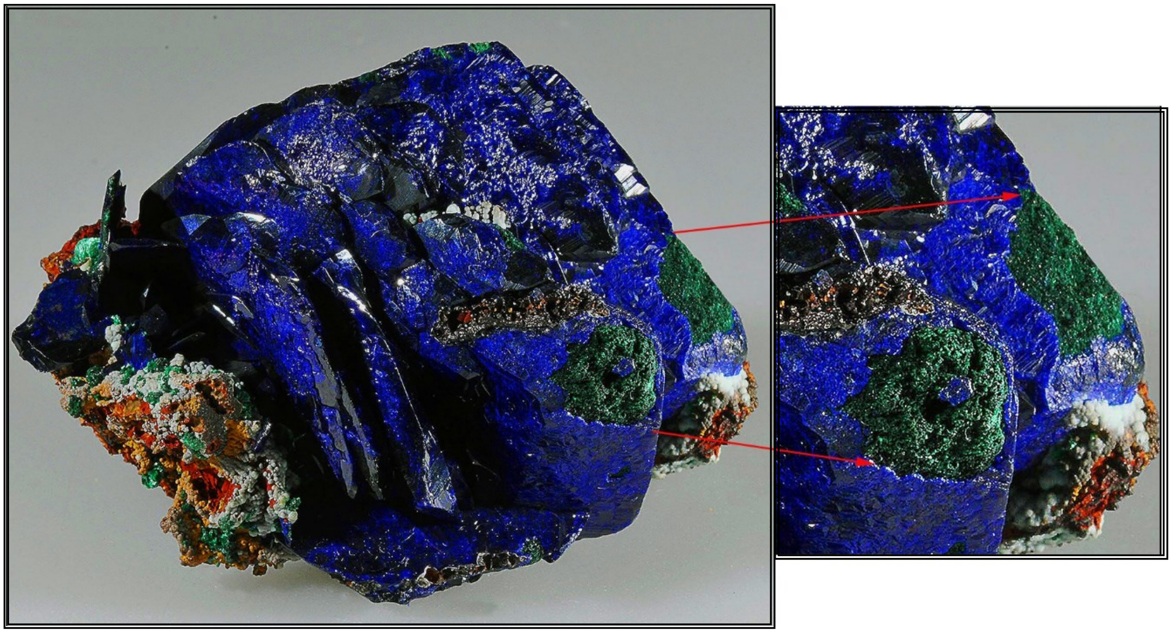
The two specimens shown below were collected the same day in August of 1970 and were less than a meter apart.



Above: Azurite as a thin epitaxial overgrowth on an exceptionally large malachite pseudomorph after azurite. The later azurite is so thin that the underlying malachite is still visible in some areas. Vertical view-10.2 cm, 105-C stope, 1900 level, Campbell Mine, Graeme collection.

Right: A malachite pseudomorph after azurite covered by a second generation of fibrous, subaqueous malachite.

Specimen- 8.4 cm, 105-C stope, 1900 level, Campbell Mine, Graeme collection.



Azurite as a near-complete, epitaxial overgrowth on tabular, malachite pseudomorphs after azurite. The interface of the azurite and the underlying malachite is crystalline and does not reflect the corrosive appearance, so typical of alteration. Specimen–6.5 cm, 200 level, Czar Mine, Graeme collection.

A second example of the overgrowth by azurite is above. This azurite crystal group from the Southwest orebody on 200 level of the Czar Mine occurred at the opposite, extreme western extent of mineralization from the previous Campbell Mine specimen. This, with the fact that all azurite crystals in-between, illustrates the district-wide occurrence of this phenomenon. A close look at the azurite/malachite interface shows crystal face development and not corrosive replacement textures, which would be evident if the azurite were altered or altering.

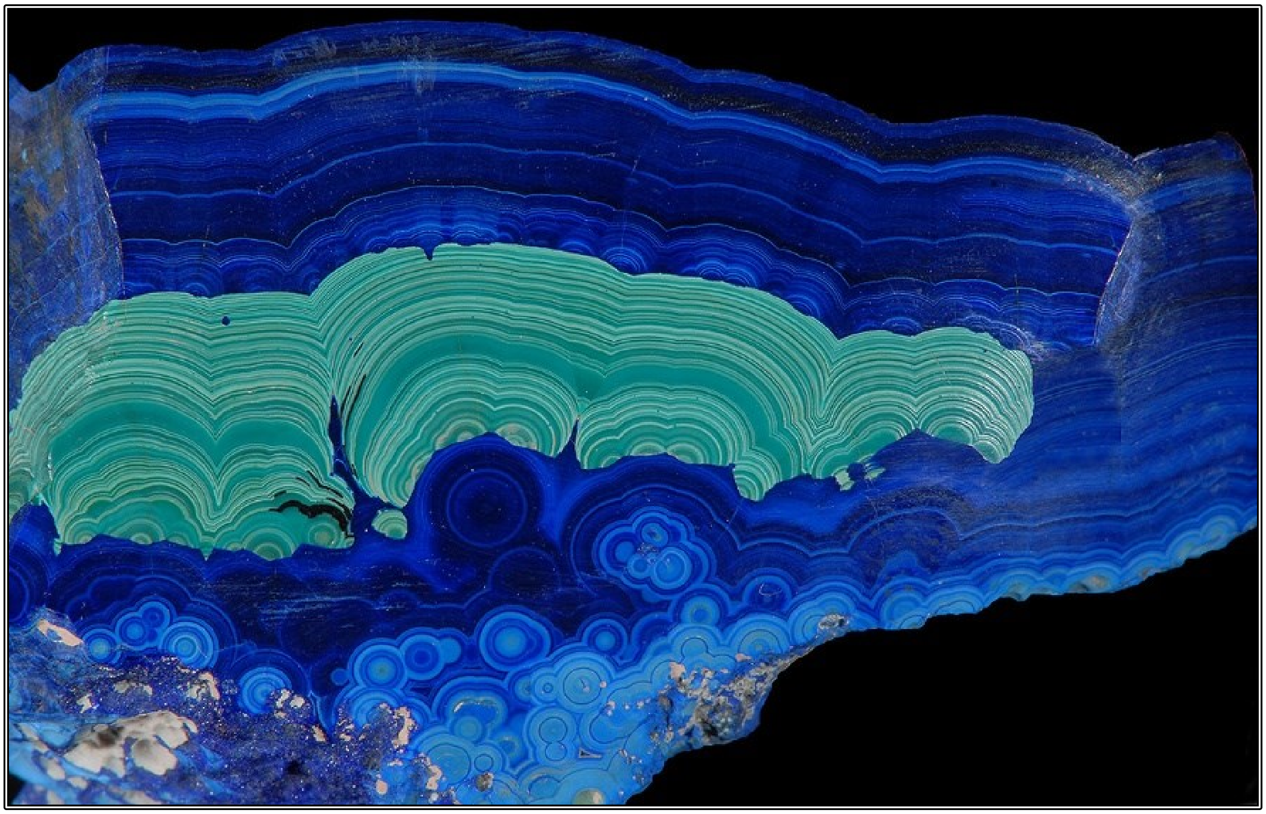
Perhaps the most illustrative of the second-generation overgrowths are the type of specimens figured to the left. Palache and Lewis (1927) studied these very types of specimens and noted:

"Apparently the pseudomorphs retain a structure adequate to control the orientation of later azurite deposited on their surface. The sequence of deposition of azurite, alteration to malachite, and later crystallization of azurite, indicates a delicate balance in the equilibrium relations."

Left: Two, malachite pseudomorphs after azurite with epitaxially oriented second-generation of azurite. Gardner Mine, Larger specimen–4 cm, Graeme collection.

Further, Palache and Lewis (1927) noted that: "*The azurite crystals are of magnificent blue color on the exterior but for the most part, when broken through, a green malachite center is visible which indicates that the second generation of azurite is also in process of alteration to malachite.*"

The specimen to the left in the above illustration has a small part of the azurite at the bottom broken, but it is all azurite. Nonetheless, the alteration of the second-generation is not a surprise as many, many malachite pseudomorphs after azurite from a number of different localities shows the complete alteration of the second-generation to malachite.



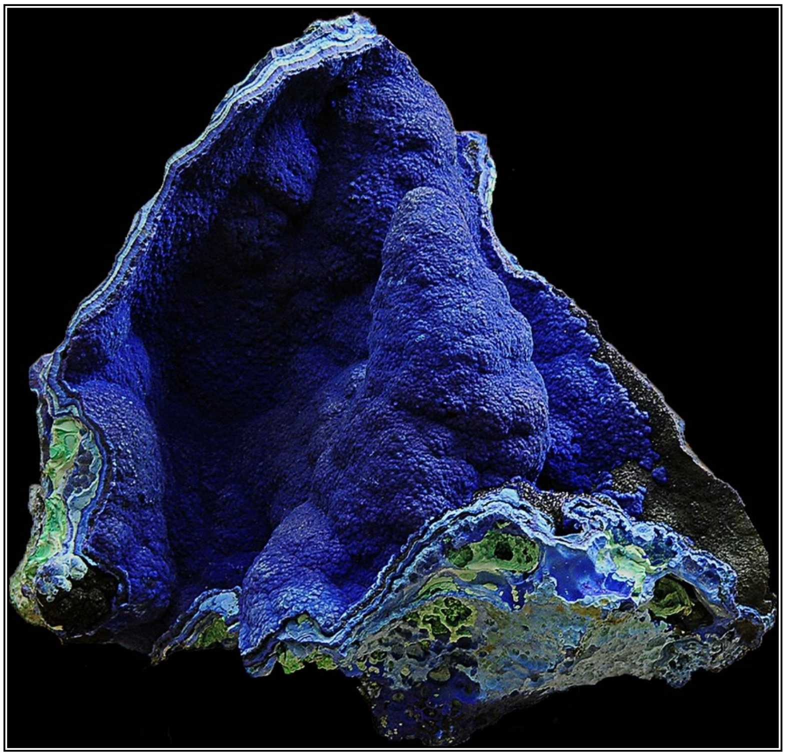
Subaerial malachite surrounded by subaerial azurite with textures suggesting partial replacement of malachite by azurite, Czar Mine, View-3 cm, Graeme collection.

Does azurite replace malachite? Little is known of the dissolution kinetics of malachite and azurite. It may be that one or other is more resistant to attack around equilibrium conditions, or for that matter, conditions where the p(CO_2) would decidedly form azurite. Azurite replacing malachite is rarely recognized. We have seen very few examples, such that as illustrated above, and even this could be debated. Vink (1986) wrote: *"Pseudomorphs of azurite after malachite seem to be extremely rare."* To us, "extremely rare" is very much an understatement.

AZURITE STALACTITES:

Bisbee has produced some incredible stalactitic masses of azurite. A small number of these classic, pre-1900 pieces grace several museums. Azurite in stalactitic form, though uncommon, was not rare. Most of Bisbee's azurite stalactites are relatively small, having formed in the voids lined with subaqueous azurite.

What seems rare, if not extremely rare, are azurite stalactites, which developed solely from the subaerial deposition of azurite.

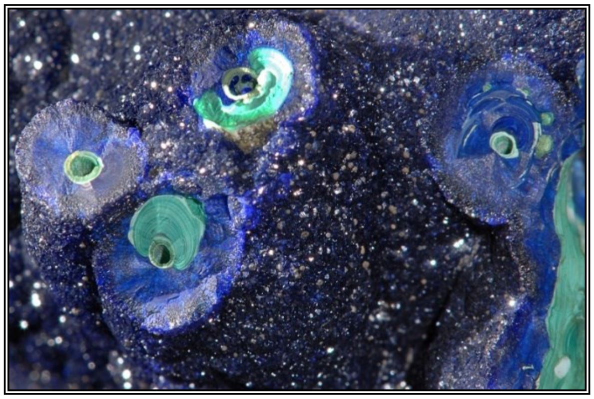


Right: An azurite stalactite, which appears to have developed in this form directly in a subaerial environment and not over a preexisting stalactitic form. When collected, the specimen simply slipped free of the Mn oxide lining the void, with no sign of the malachite that is present forming, anything other than a thin coating. Holbrook Mine, specimen–10.5 cm, Graeme collection.

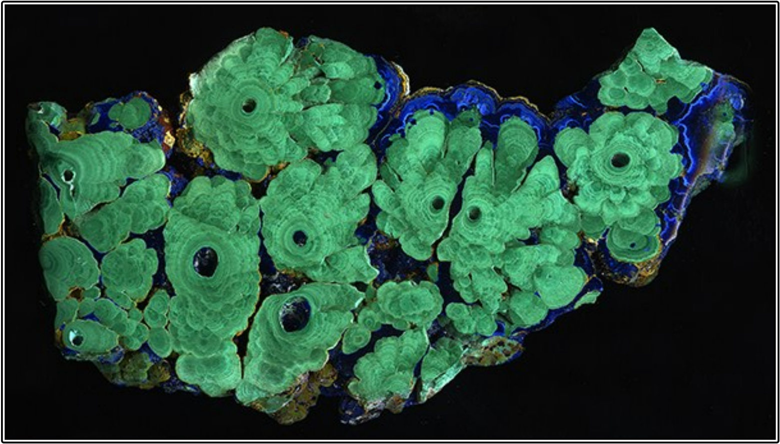
Of the several dozen examples of Bisbee azurite stalactites we have studied, all but two are definitely azurite overgrowths of preexisting stalactites, such as over malachite, goethite, or gibbsite stalactites. Those few that perhaps formed directly as stalactites are like the example to the right, where one cannot definitely see from the base if other species may be in the core.

Both subaerial and subaqueous overgrowths have been recognized, with subaqueous far more common—the latter case reflecting a change in the environment from open-air to solution-filled space. Not surprisingly, we have noted azurite, which had coated a malachite or another mineral stalactite completely altered to malachite. Partial coatings of stalactites by azurite, usually as crystals from a subaqueous environment, were not as rare as stalactites fully coated.

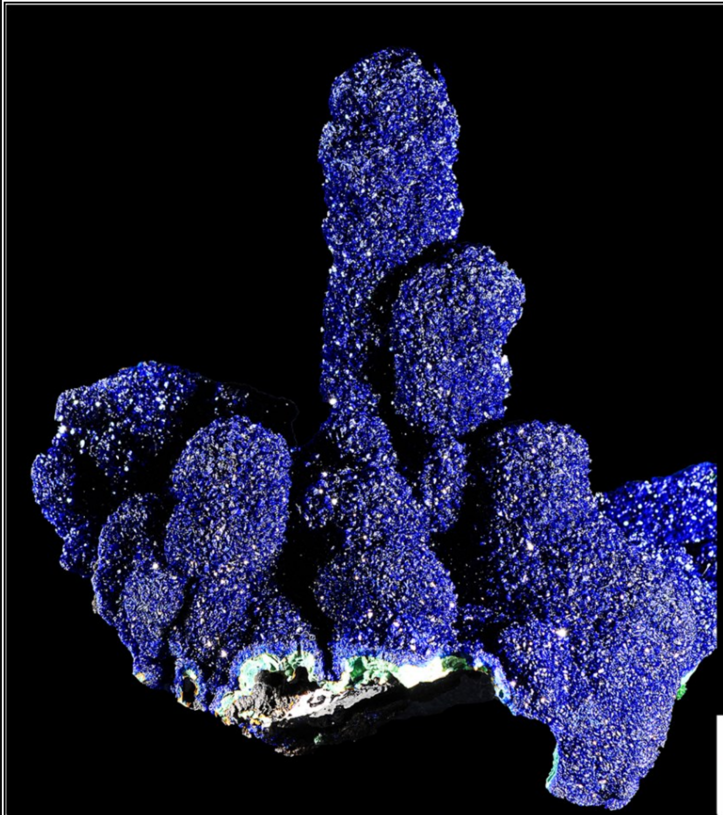
In very few instances, the azurite overgrowing the other mineral stalactite has, in turn, been coated by malachite. This later malachite has always been subaqueous in deposition, in the few examples seen. These make stunning slabs when otherwise too damaged for specimen preservation.

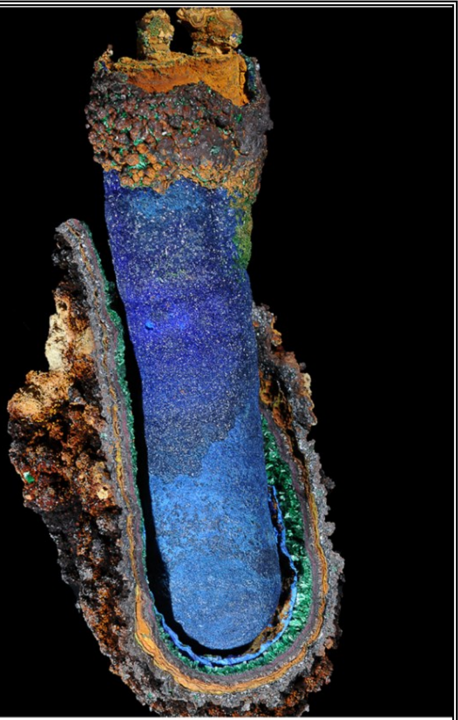


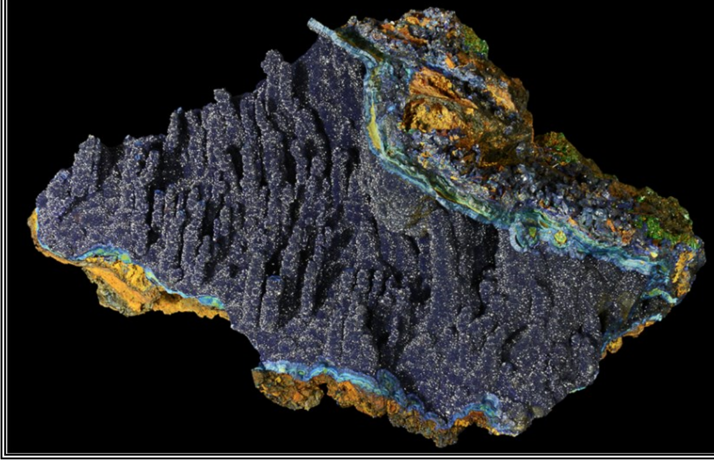
Right: Broken, azurite stalactites, showing the cores of malachite stalactites over which, they formed in a subaqueous environment. Holbrook Mine, view–3.6 cm, Graeme collection.



Left: Polished malachite and azurite stalactite section, specimen-9 cm, Holbrook Extension, Lavender Pit Mine, Graeme collection.



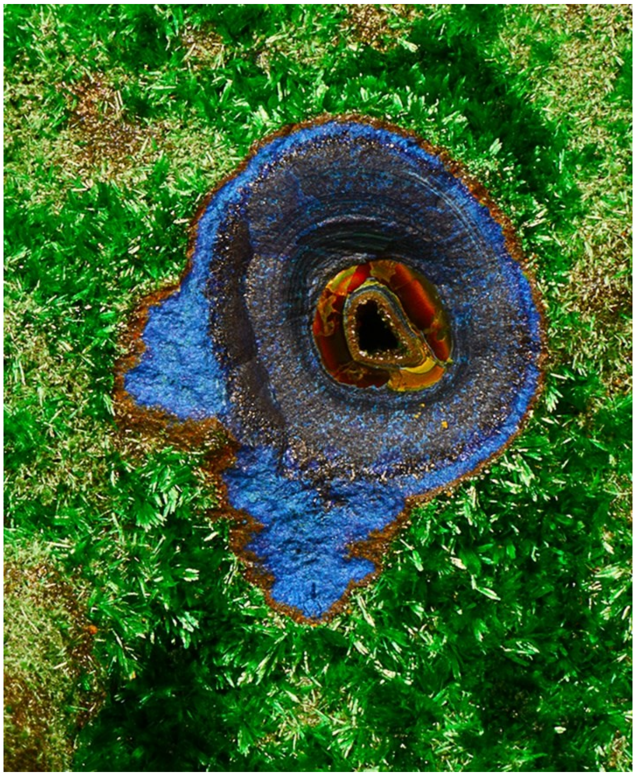




Top left, azurite as a drusy, subaqueous overgrowth of a malachite stalactite, specimen-6.5 cm, 1400 level, Sacramento Mine, Graeme collection.

Above, azurite as a thin, subaqueous coating of a goethite stalactite, which was overgrown by suaqueous malachite and later, a crust of subaerial goethite, reflecting fluctuating depositional environments of several phases, with changing solution chemistry, specimen-10.8 cm, Sacramento Mine, Graeme collection.

Left, azurite as a drusy, subaqueous coating of thin, 1.2 cm long, goethite stalactites, specimen-10,1 cm, Czar Mine, Graeme collection

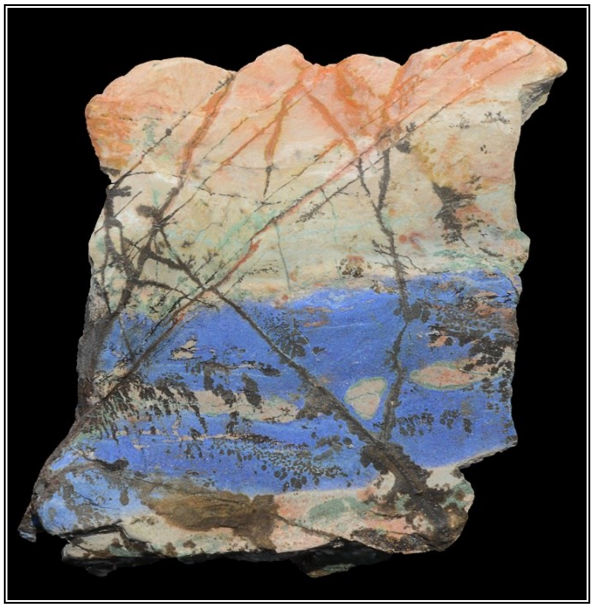


An azurite stalactite which formed around a goethite-lepidocrocite stalactite in a subaqueous environment, then coated by goethite on malachite coated goethite. View -2 cm, 45 raise, 200 level, Shattuck Mine, Graeme collection.

We have no explanation for the apparent reluctance of azurite to form stalactites, as its sister carbonate, malachite, readily does so under what are apparently near-identical conditions. Gel deposited stalactites are commonly seen in malachite, goethite, allophane, chrysocolla, and other minerals. Malachite stalactites, which are quite common, seem to have formed from a less viscous solution.

The vast majority of azurite mined at Bisbee was ore-type material. It was unimpressive, massive material intimately mixed with iron oxides, usually with malachite or, less often as earthy azurite, almost grain for grain replacement of altered limestone. Examples of both are shown below.

Typical high-grade carbonate ore, > 7% Cu, composed of copper carbonates in a mix of clays/claylike minerals, goethite and altered limestone. 14 stope, 5th level, Southwest Mine, specimen-20 cm, Graeme collection.

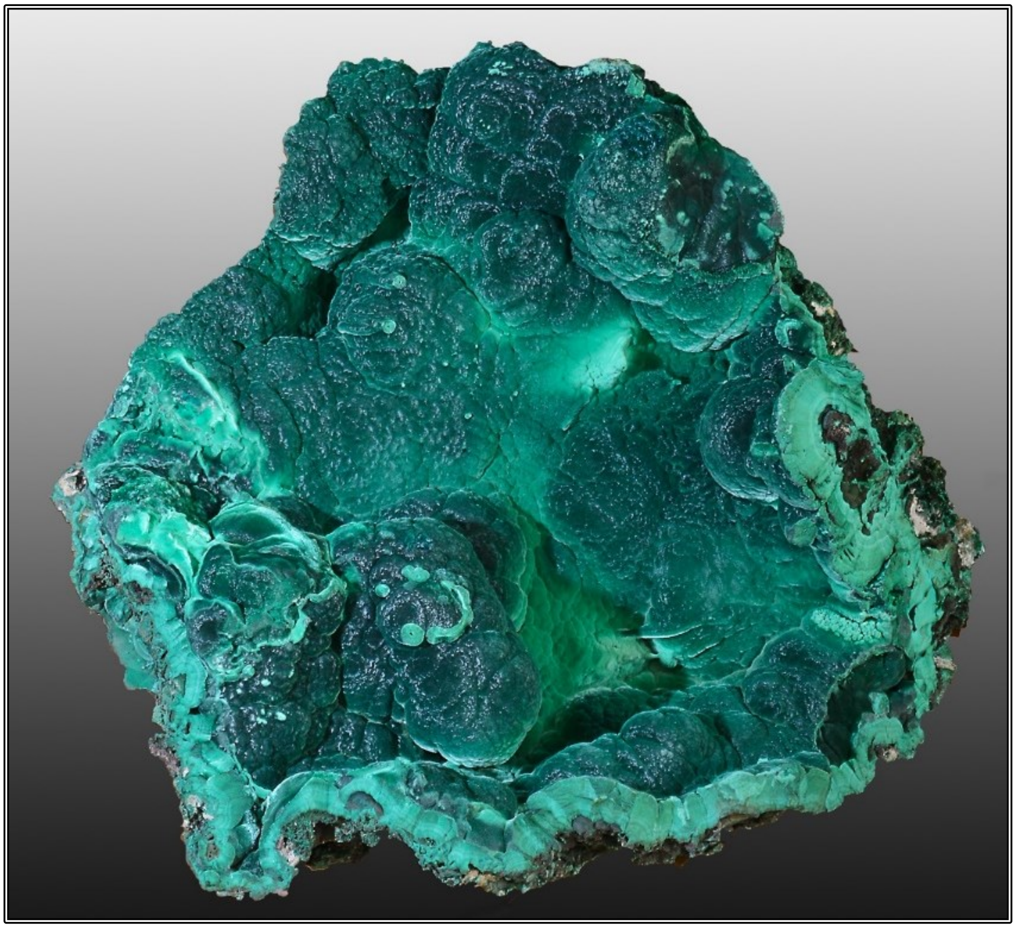


Average grade carbonate ore, ± 5% Cu, as azurite replacement of altered limestone, specimen-8cm, 600 level, Shattuck Mine, Graeme collection.

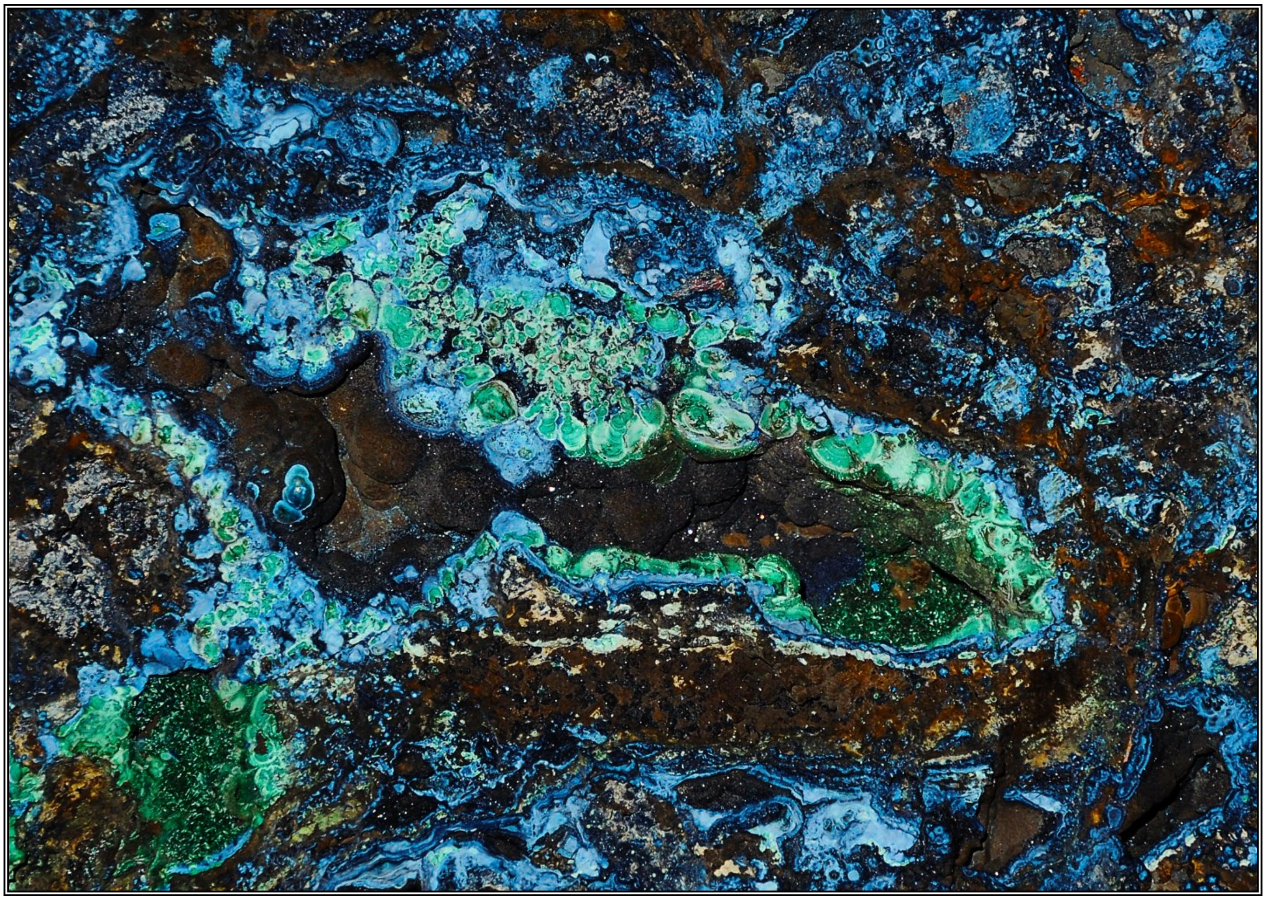
MALACHITE:

Malachite was literally everywhere supergene activity had occurred in the limestones. It is one of the most stable copper minerals under near-surface conditions. This mineral occurred in a wide variety of forms and hues of green and was far more common than azurite. James Douglas, in his classic 1900 paper on the Copper Queen Mine, described malachite as found at Bisbee and its typical occurrence. He wrote that:

"The Copper Queen mine has become famous for its beautiful specimens of carbonates, both malachite and azurite. The malachite is never found in such large and compact masses as to make it commercially valuable for decorative purposes; beside being generally thin botryoidal masses, it is usually streaked with manganese, which detracts from its purity. Its most striking mode of occurrence is in geodes, which are lined with velvety crystals of the same material. These hollow spheres, the walls of which are composed of concentric layers, are rare, but, when found are usually in nest embedded in soft wet, ferruginous or manganiferous clays, such as constitute the gangue, or "ledge-matter," of nearly all the ore; and they occur at no great distance from a limestone wall or partition."



Malachite "geode" as described by Douglas, (1900). When collected, it was lined with soft, acicular crystals to 7 mm long, which suffered damage while handling the unwieldy, 22-kilogram mass and were removed by washing. Czar Mine, specimen 35 cm, Graeme collection.



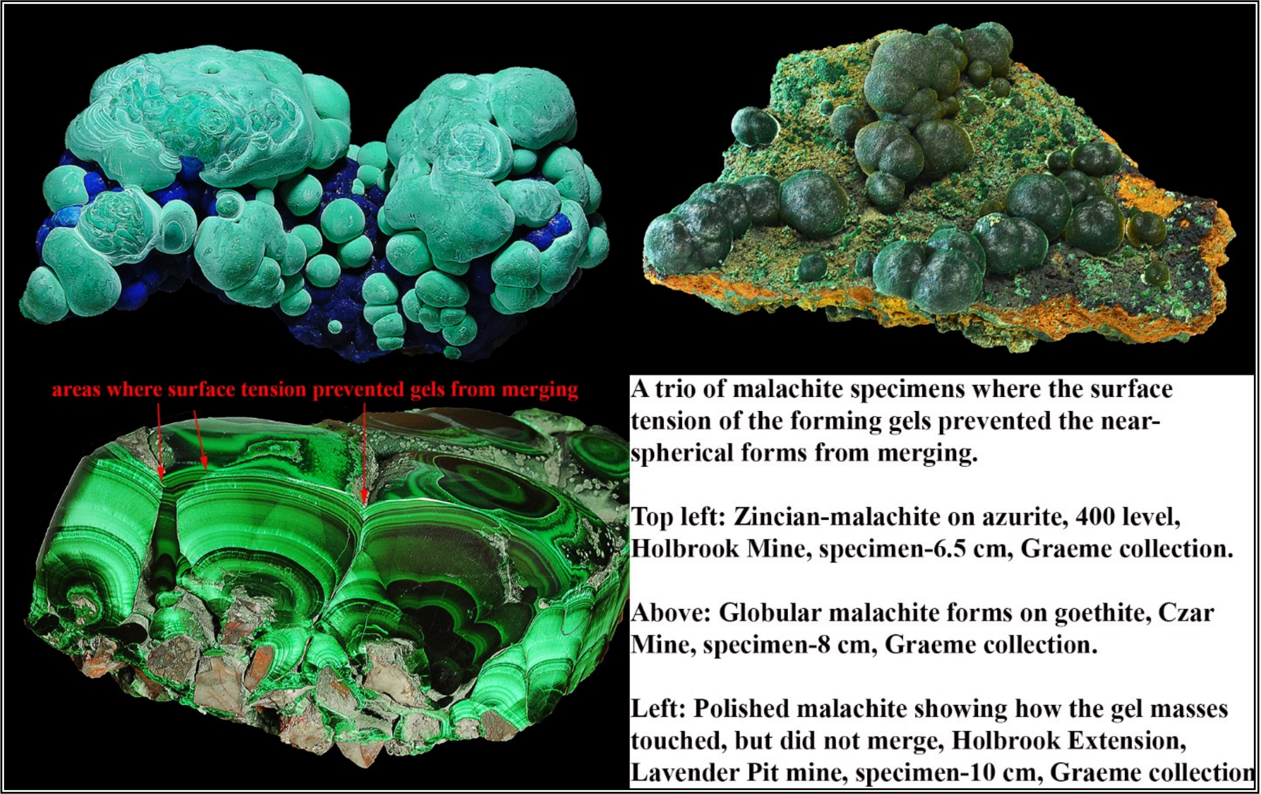
Reniform malachite and azurite vug in the 3½ ton block in the American Museum of Natural History. The image has been rotated to reflect the approximate position during formation. Horizontal view ≈ 40 cm., 200 level, Czar Mine.

DEPOSITION:

As previously noted, malachite too forms under subaerial and subaqueous environments, and just like azurite, the subaerial forms develop as a gel, as well as in decidedly less viscous solutions. It is the gel origin that gives malachite its often globular form. The surface tension between the individual gel masses often prevents them from joining and, while they may touch, they frequently do not merge.

This is clearly shown in the above illustration of a ± 35 cm vug in the large block of azurite, malachite, and goethite in the American Museum of Natural History. Note the vug is lined with globular malachite and, to a lesser extent, similar azurite, resulting in an overall reniform surface. A thin veneer of goethite has coated much of the vug surface, except for a small area of later subaqueous malachite, which can be seen as bright, acicular crystals in the vug bottom to the far right. No doubt, this malachite sits on the thin goethite layer.

Subaerial, gelatinous deposited malachite is found as rounded blobs to several centimeters in size, while the subaqueous malachite had formed as distinct crystals, almost always acicular.



A trio of malachite specimens where the surface tension of the forming gels prevented the near-spherical forms from merging.

Top left: Zincian-malachite on azurite, 400 level, Holbrook Mine, specimen-6.5 cm, Graeme collection.

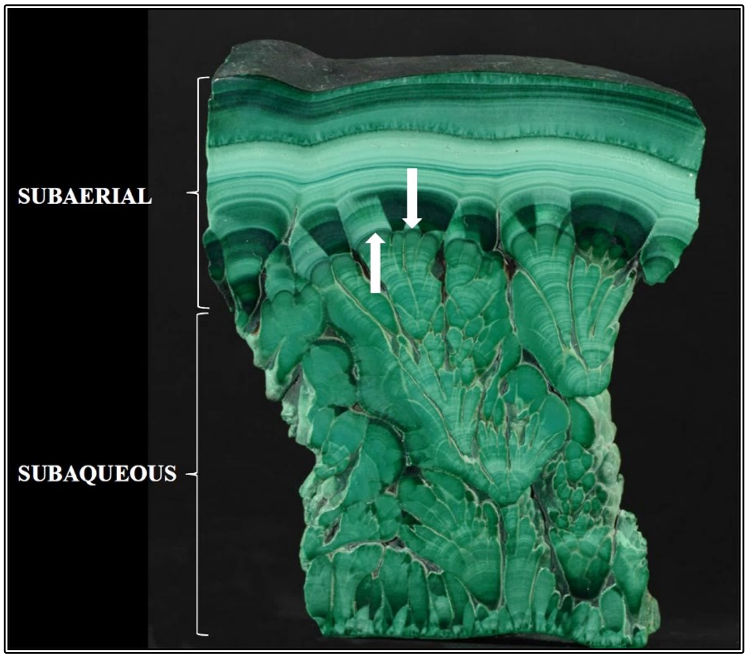
Above: Globular malachite forms on goethite, Czar Mine, specimen-8 cm, Graeme collection.

Left: Polished malachite showing how the gel masses touched, but did not merge, Holbrook Extension, Lavender Pit mine, specimen-10 cm, Graeme collection

The subaqueous malachite crystals are almost always closely clustered acicular crystals. Occasionally, these formed plumose clusters to several centimeters in length. But it was the acicular crystals scattered in the clays or lining voids that were the most common and most important oxide ore mineral. An example is shown below.

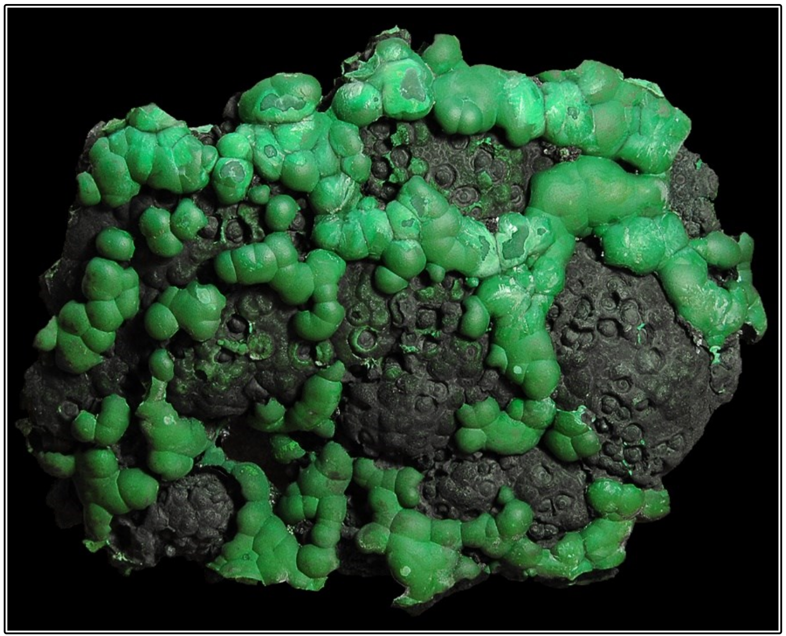
Left: Malachite in its most common form at Bisbee; as acicular crystals. This is an uncommonly fine specimen of the type. The crystals are up to a centimeter long and of subaqueous origin on a dense, quartz/hematite matrix, with minor cuprite, specimen-9 cm, Holbrook Extension, Lavender Pit Mine, Graeme collection.

Large, blocky crystals are known from a few localities but are exceeding rare at Bisbee. These blocky crystals are often called "primary," indicating that they are not pseudomorphs. This is less than ideal; they are just malachite.



Right: Compact, banded, subaerial malachite overgrowth of somewhat open, plumose, subaqueous forms. Specimen-10.7 cm, Holbrook Extension, Lavender Pit Mine, Graeme collection.

Fluctuating solution levels cause overgrowths of one form over the other, but this is far less obvious than with azurite overgrowths. Subaerial malachite is often banded as well, so banding alone is not a perfect indicator of the depositional environment. The common gel-related features are more telling. So many malachite specimens show the fluctuation between the subaerial - subaqueous type depositional environments that they are the rule rather than the exception. Indeed, it is quite common to see indications of several such episodes at varying levels in a single specimen. Absent distinct depositional features, such as stalactites, it is often difficult to discern, with certainty, that one or more fluctuations in the depositional environment had occurred.



Malachite from a subaerial depositional environment on an earlier malachite of subaerial origin, showing the influence of the now removed Mn oxides on deposition. Minor calcite is on the malachite Specimen-12 cm, Holbrook Extension, Lavender Pit Mine, Graeme

Malachite stalactites in a vug, somewhat-bent, showing localized malachite deposition from a subaqueous event controlled by Mn oxides. Horizontal view-10 cm, Czar Mine, Graeme collection.

The presence of other minerals, notably Mn and Fe oxides, controlled the deposition of malachite, much as it did azurite. This has happened in both subaerial and subaqueous environments. Numerous specimens show this feature, but washing has generally removed the soft Mn oxides, leaving only the malachite. The resulting forms are interesting and give an additional dimension to the interesting malachite forms.

Malachite as a replacement of crinoid stem segments on Mn oxide coated malachite and azurite. The reverse is sprinkled with azurite replacements of crinoid stem segments, but is somewhat crystalline and less distinct.
Horizontal view-6.2 cm, Holbrook Mine, the formation was in the Mississippian age Escabrosa limestone. Graeme collection.

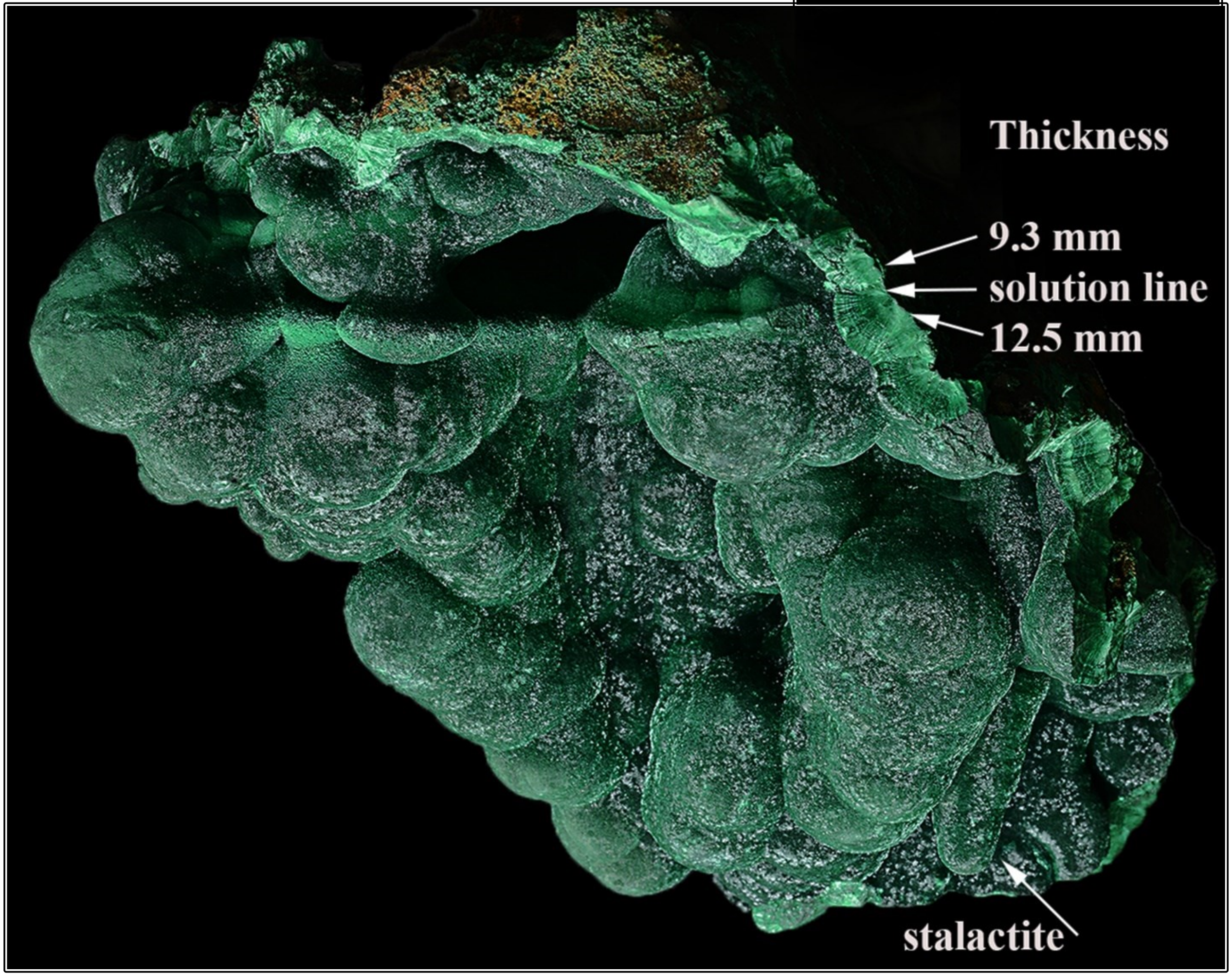
Malachite, like azurite, was commonly found as an in-situ partial to complete replacement of the hosting limestone. Occasionally, even carbonate fossils were replaced. The last oxide orebody being mined at the time of shutdown was of ore-grade by the many fossil *atripas* replaced by soft azurite. The azurite was so soft; it could not be removed as a specimen, while the matrix, mixed azurite and iron oxide, was clay-like and quickly decrepitated when dry. No specimens have survived. Silica fossils are commonly seen as capture inclusions in and on the copper carbonates.

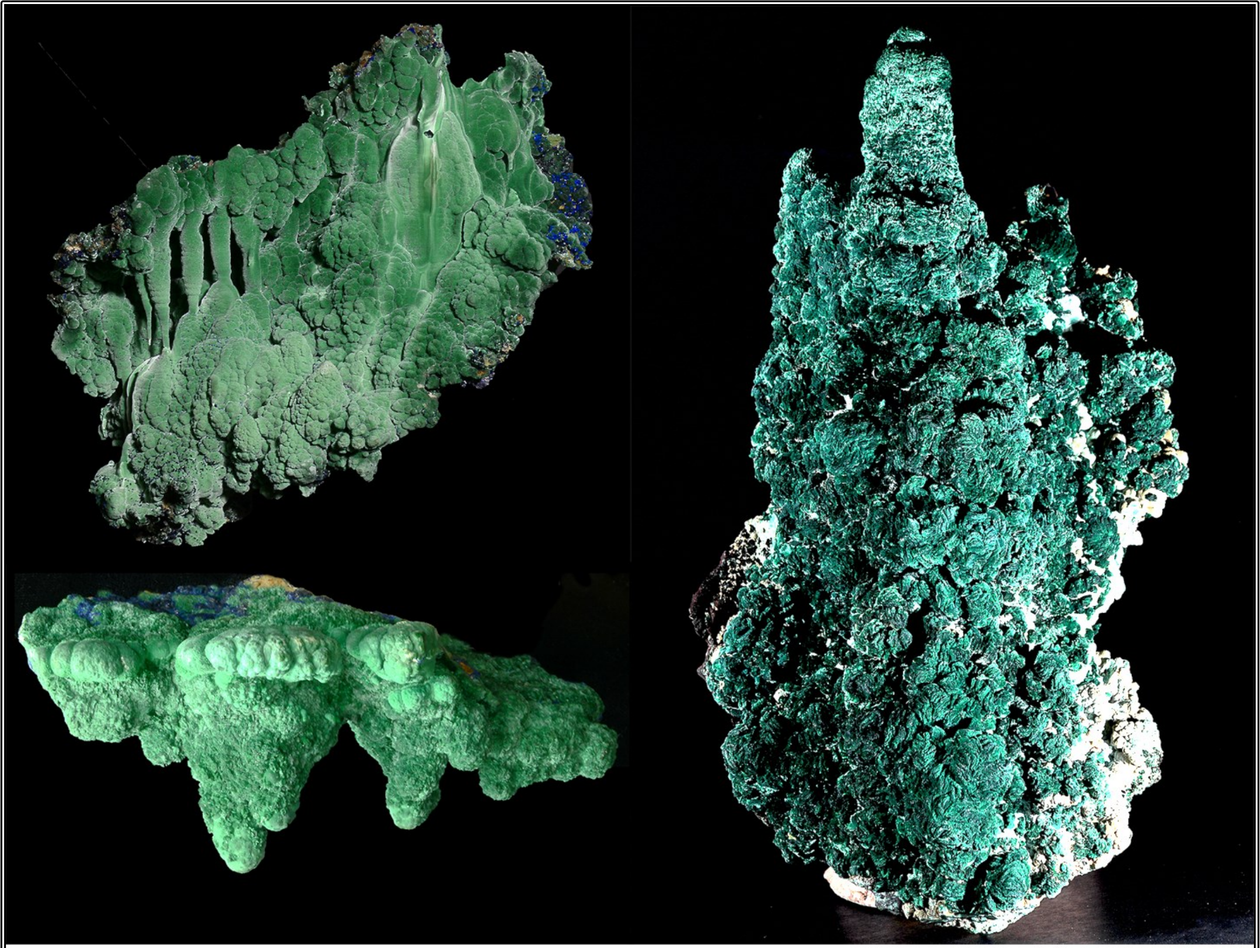
MALACHITE STALACTITES:

Malachite stalactites were common at Bisbee. We have collected these forms starting at the 1200 level Campbell Mine (1,160 meters AMSL) in the east to 7th level Southwest Mine (1,740 meters AMSL) at the west end. It is worth noting again that the malachite stalactites in the eastern part of the district were perpendicular to the bedding and not vertical, indicating their growth was pre-tilting. All others were more or less vertical, with the exceptions of those which show some bending when still gel-like. Despite the abundance of these malachite stalactitic forms, good specimens are uncommon, and great specimens are limited to but a few.

Right: Malachite as a hard, hallow stalactite. Czar Mine, specimen-9 cm, Graeme collection.

Malachite vug, oriented to the position as found, showing features common to both subaerial deposition – stalactite – and subaqueous deposition – solution line. The difference in malachite thickness above and below the solution line is 3.2 mm. No visible difference is obvious between the malachite above and below the solution line.
When collected in 1964, it was completely closed and wet, probable from ground water, as the liquid was not viscous at all. 200 level, Czar Mine, specimen 15.7 cm wide, Graeme collection.





Three typical types of malachite stalactite environments
Top left: Malachite lined pockets and vugs often contained small stalactites such as these on this 19 cm, Czar Mine specimen, which also has some subaerial azurite. Graeme collection.

Bottom left: Orebodies had openings of a meter or more, because of volume reduction during supergene activity. These frequently contained malachite as stalactites such as these 5-7 cm examples. Also, the specimen exibits a ruffeled solution line and is covered with wart-like malachite pseudomorphs after azurite. Minor amounts of azurite remain above the solution line.
From 45 raise, 200 level Shattuck Mine, Graeme collection.

Right: A large malachite stalactite group with later malachite as pseudomorphs after azurite; all on halloysite. This is from a small oxidation cave in the Holbrook Mine, which had meter-long stalactites, specimen 30 cm high, Graeme collection. Malachite stalactites in oxidation caves were rare.

MALACHITE REPLACEMENTS OF AND PSEUDOMORPHS AFTER OTHER MINERAL SPECIES:

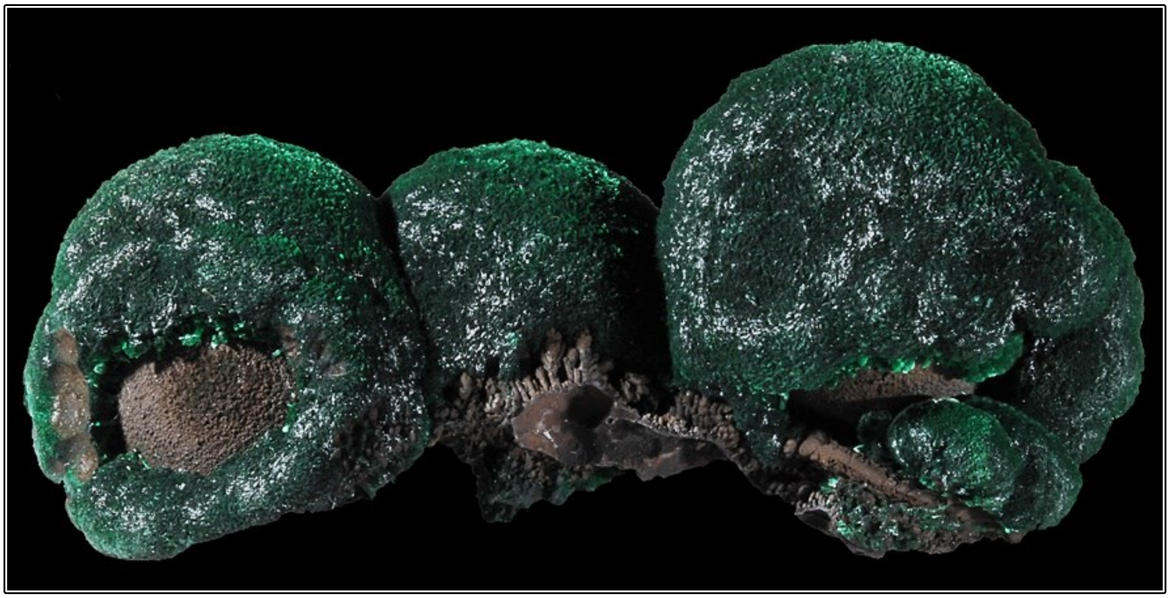
Malachite is one of the most stable copper minerals in a near-surface/surface environment. Only chrysocolla is more so, but the Bisbee supergene deposits are relatively silica poor. Thus, little chrysocolla formed at Bisbee. Chrysocolla, while common, is not abundant. Malachite is the general endpoint for supergene alteration, mainly through the alteration/replacement of a number of copper minerals.

From a collector's point of view, the most interesting replacement by malachite is as a fine pseudomorph after azurite. Truly superb malachite pseudomorphs after azurite as elongated prisms with a wedge-shaped termination are the most commonly recognized.

Right: Malachite pseudomorphs after azurite. Specimen-14 cm wide, 1022 XC, 1300 level Campbell Mine, Rice Museum collection, Jeff Scovil photo, used by permission.

Collected by miner Angel Salas in February, 1948, traded to barber Esker Mayberry and in turn sold by Esker to Richard and Helen Rice with the whole of his collection in 1967.

Indeed, it is our collective opinion that the incredible malachite pseudomorph after azurite from the 1300 level of the Campbell Mine, shown above, is not just the finest such pseudomorph from anywhere, but the best mineral specimen from Bisbee. At this writing, it resides in the Rice Museum.

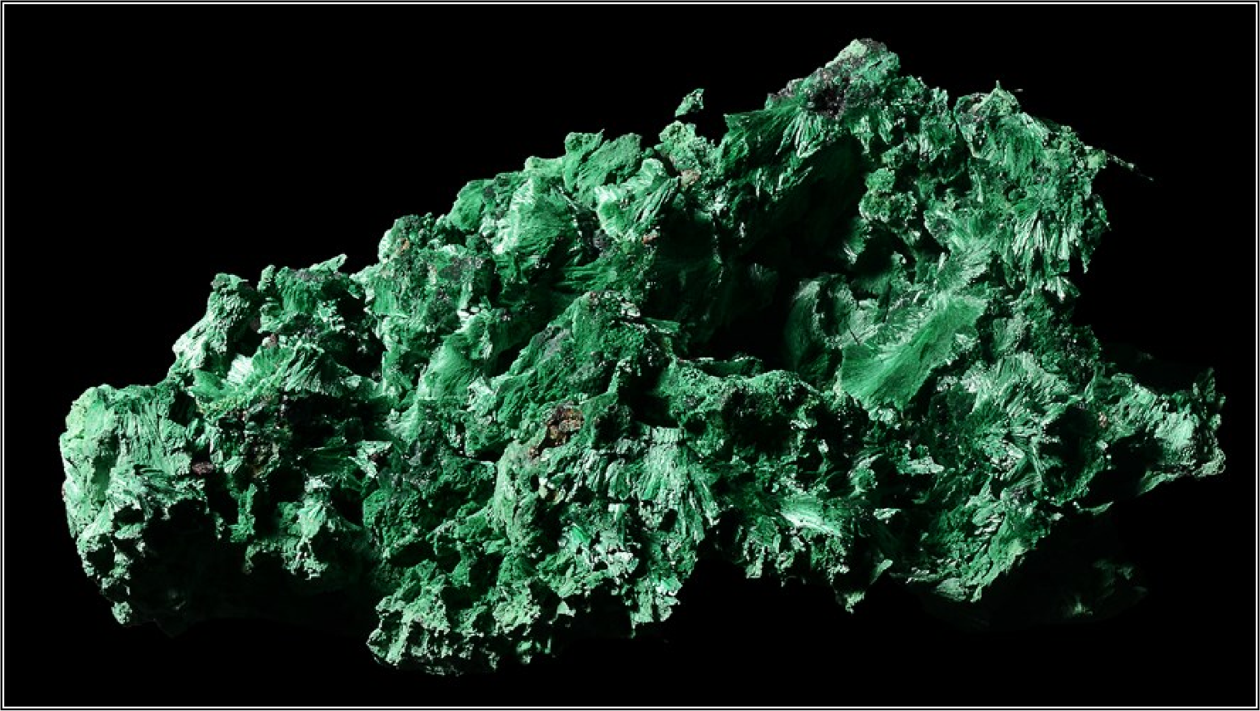


Malachite replacement of azurite, which had been deposited as a thick cryptocrystalline partial, crust on Mn oxide coated malachite. As seen in other specimens, the presence of Mn oxide controlled the deposition of azurite, 400 level, Gardner Mine, specimen-8.5 cm, Graeme collection.
When collected from a small opening in the oxidized ores, it weas completely covered with delicate, hair-like malachite crystals to 5 cm, which broke at the touch. These were removed by pressure washing.

Malachite pseudomorphs after azurite were almost everywhere and, as previously noted, in almost every form in which azurite had formed.

Malachite pseudomorphs after other species are few and largely unimpressive, with minimal exceptions. Strikingly good malachite pseudomorphs after large brochantite crystals were mined from the Uncle Sam Mine during the 1920s, and some fine malachite pseudomorphs after copper were found on the 1200 level of the Cole Mine in the 1960s. An example of the latter is shown below

Malachite pseudomorphs after spinel twin copper crystals on calcite in boxwork goethite. 1200 level Cole Mine, specimen-11 cm, Graeme collection.



Malachite as silky, lustrous, acicular crystals in divergent sprays, which formed as a direct, in-situ replacement of massive chalcocite in a subaqueous environment. 6th level, Southwest Mine, Specimen-20 cm, Graeme collection

The in-situ replacement of chalcocite by malachite was particularly common in many of the district's mines. This ranged from thin veneers along fractures to complete replacement, resulting in large masses to a meter in size of jackstraw malachite crystals. These were often silken to splendent in luster, which with the often-erratic forms created unusual and fine specimens. The larger malachite crystals formed during this replacement can easily be mistaken for brochantite.

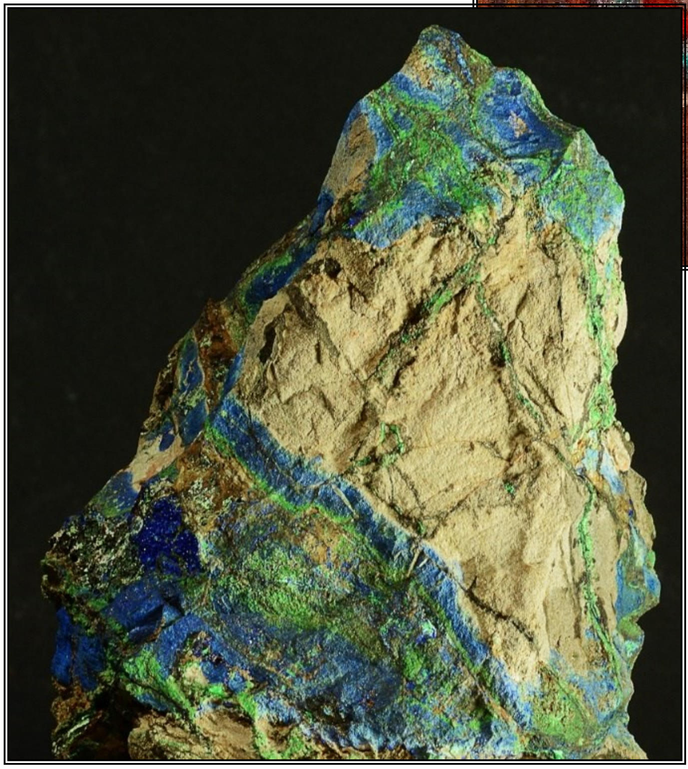
Right: Exceptionally large malachite crystal formed by the direct, subaqueous and in-situ replacement of chalcocite by malachite. Holbrook Mine, specimen-7.5 cm, Graeme collection.

MALACHITE AS ORE:

As with azurite, most malachite mined as ore was of little interest as specimens. We truly doubt that much in the way of anything, even remotely interesting, left any of the mines as ore. Good specimens always had a value at Bisbee, and the miners were allowed to collect and keep whatever they found, a most enlightened policy.

While discussing the ores mined, Douglas (1900) wrote: *"The oxidized copper-ores, however, which were mined in economic quantities, consist usually of cuprite and carbonate, disseminated through limonite; or of carbonates, chiefly of the green variety, in streaks or crystals scattered through ferruginous or manganiferous clays…"* An example of such ore is illustrated below. This area was mined before 1888.

Right: Malachite, as acicular crystals lining goethite vugs in iron-rich clay-like materials. This was very typical of the carbonate ores. View-1.2 meters, "B" level, Copper Queen Mine. Graeme/Larkin collection.



Left: Azurite and malachite as a replacement of altered limestone. This is of ore grade at 7% Cu. View-6.2 cm, 600 level, Shattuck Mine. Graeme collection.

OXIDATION CAVES

Caves, caves and more caves! Is how a miner who worked underground at Bisbee from the mid-1880s until 1945 described working in the Holbrook Mine to one of the authors in the early 1950s.These magically beautifully openings were both a boon and a bane to the miners.

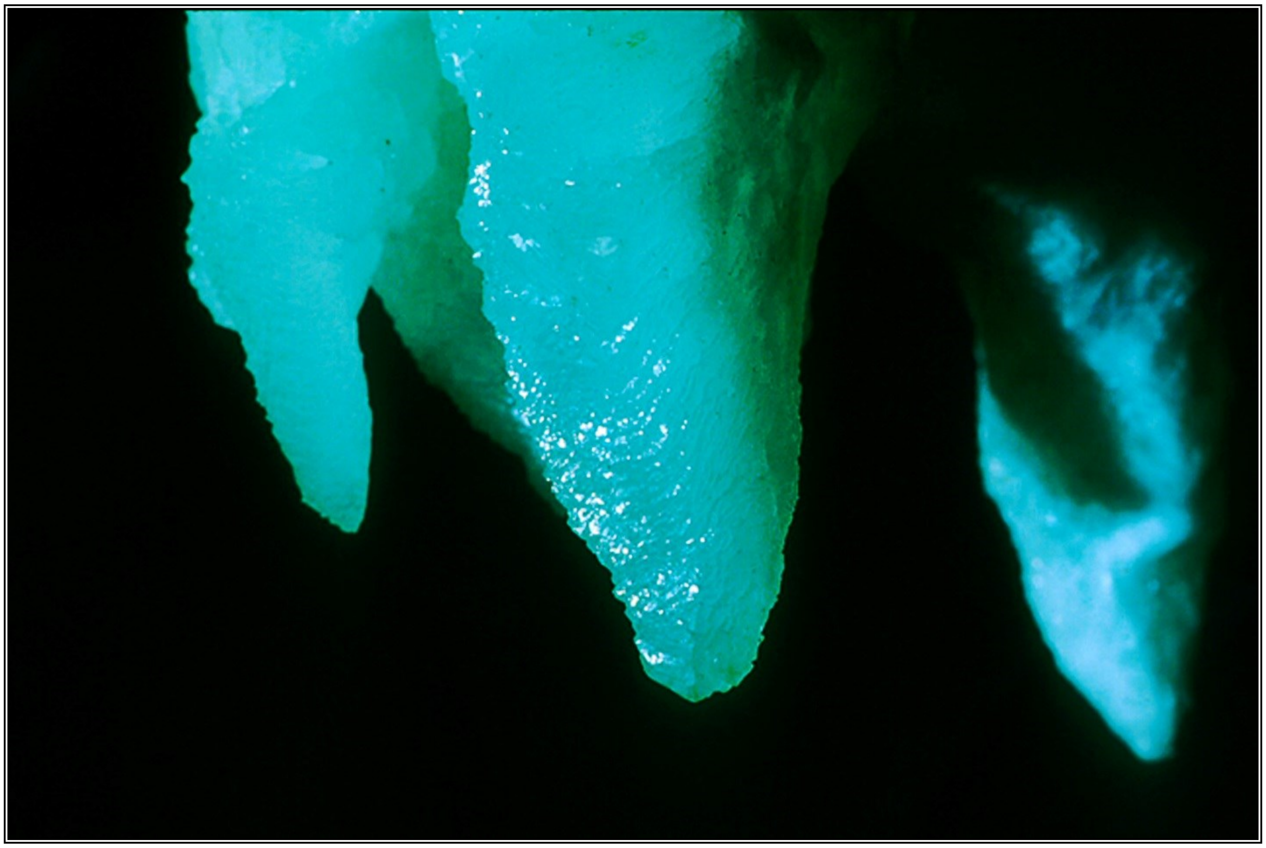
A cave brought with it more ore, ore to a mine that never had more than a few years' worth in sight during the near century of operation; something always welcome. However, with a cave always came difficult if not treacherous mining conditions. Broken rock above and sticky, unstable clays below made the recovery of what were invariably high-grade ores a challenge. And too, more waste had to be mined nearby to fill this additional hole.

A classic oxidation cave just above the 100 level, Holbrook Mine. One of the authors, (DLG) at the bottom-center is actually 45-meters above the cave floor. Graeme/Larkin collection.

Authors' note: The following is largely a modified excerpt of our 2016 book, The Forgotten Caves of Bisbee, Arizona, which explores the history in-depth and with more on their genesis.

Perhaps, the least know and least understood in terms of Bisbee's minerals are the caves associated with the completely oxidized ores in the western part of the district. Hundreds of oxidation-formed caves were found while mining the rich oxide copper ores in Bisbee during its first 50 years of operation. Many fine mineral specimens were recovered from these openings and the ores below.

Often these openings were beautiful beyond description, as they were typically well decorated, but there was more. In many of the caves, some of the speleothems, such as stalactites, stalagmites, and other cave formations, were stunningly tinted in varying hues of blues and greens by the ever-present copper. On rare occasions, nearly the whole cave contained formations so colored (Beasley, 1916). This remarkable coloring was invariably complemented by a striking red-brown hue in some speleothems because of iron oxide inclusion, creating a handsome contrast with the other, mostly white formations. During mining, thousands of attractive specimens were recovered, truly salvaged from these magnificent openings, which by necessity, would be destroyed. Few of these specimens survive today, and fewer are displayed because of the appropriate desire to protect cave speleothems by not presenting them as a desired collectible.



Calcite stalactites tinted green by copper. Minor malachite is also on and included within the calcite, 5th level, Southwest Mine, view – 34 cm. Graeme collection

The total number of oxidation caves discovered during mining is not known. The authors estimate that hundreds and perhaps, in excess of a thousand oxidation caves of all sizes were found in Bisbee between the start of mining in 1880 and exhaustion of completely oxidized ores circa 1930.

Stalactites and helictites tinted by copper and iron. Calcite is colored green by copper or red-brown by iron, while aragonite is tinted blue-green by copper, 100 level, Holbrook Mine, view–5 meters. Graeme/Larkin collection.

The geneses of these natural wonders were confusing. No one had an explanation as to how rich mineral deposits in limestone such as found on the Copper Queen claim formed. They were rare, and, at the time, the geology was poorly understood. No one could conceive of a way for such rich ores to have formed in otherwise seemingly barren limestone. Ideas regarding the replacement of limestone by mineralizing fluids, such as happened at Bisbee, were just evolving, and the concept of the oxidation of sulfides and related processes was far from universally understood or accepted.

OXIDATION CAVE DEVELOPMENT:

The early views of how the Copper Queen Orebody formed were founded in geologic concepts of very different deposit types. Dr. James Douglas, a man of some note in the copper business of the era, wrote the first account of these ores and of a cave in 1881.

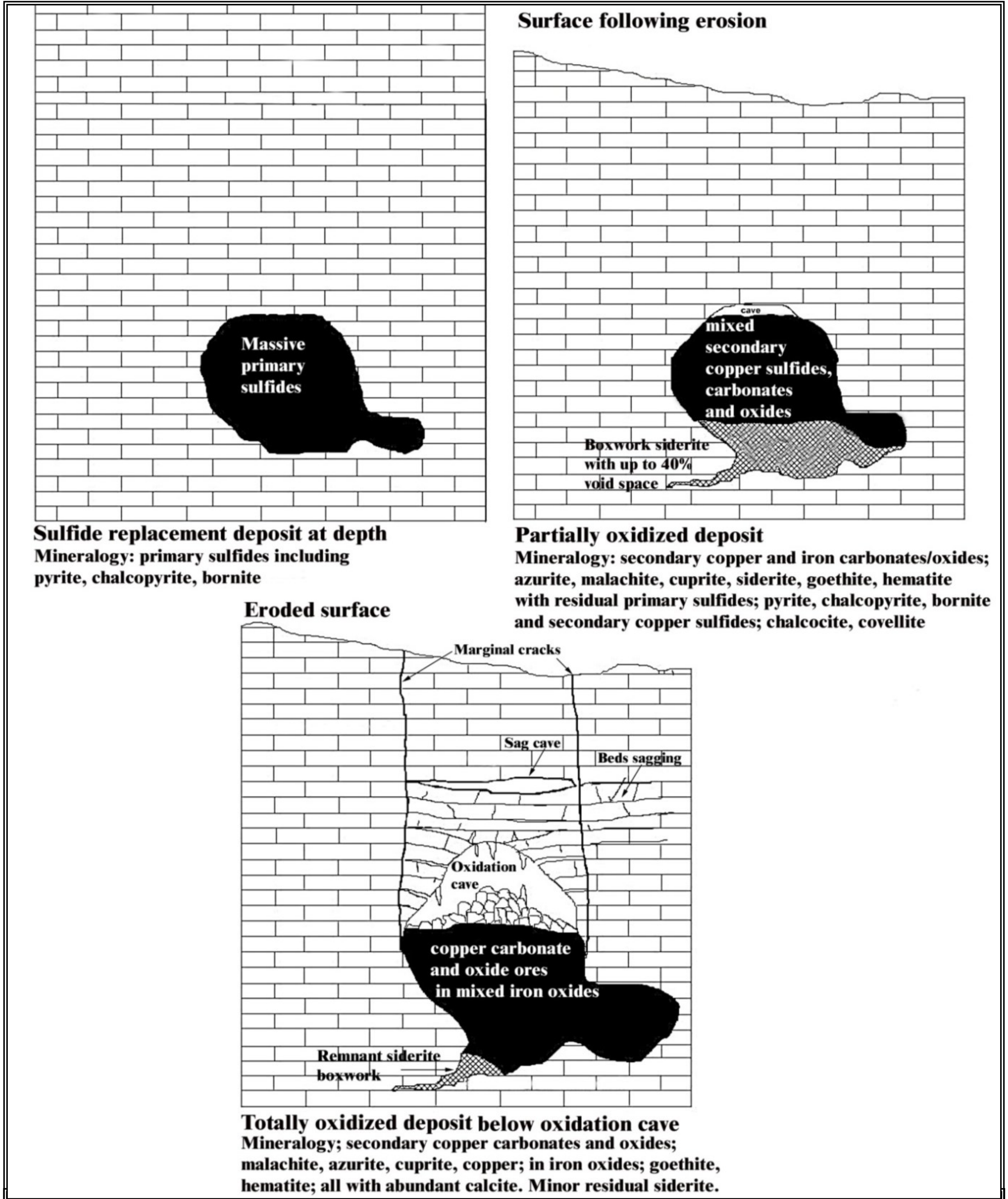
> *"... I think that it was a cave, only a very large one, which received, this mineral, that now makes the Copper Queen a mine, and that its occurrence as a carbonate is due to the limestone, which originally carried it and from which it filtered into this reservoir. This conjecture be correct, there is no reason to suppose that sulphurets* [sulfides] *will be found."* (Douglas, 1881)

Others of the era (e.g., Wendt, 1887a) came to much the same conclusion that pre-existing caves had been mineralized. Even though this is not what happened at Bisbee, it was a valid concept for similar-appearing deposits such as those at Leadville, Colorado and Tintic, Utah.

Now such deposits are widely recognized, and the fact that sulfide mineral deposits have been emplaced in pre-existing caves was long accepted. Examples abound throughout the world of paleokarst environments hosting sulfide ores (Morehouse, 1968, Palmer, 1991; Quinlan, 1972; Walker, 1928). The deposition of sulfide minerals in hypogenic caves (hydrothermally developed) is equally well documented and accepted with the extensive lead/zinc deposits of the Picher Field in Oklahoma and Kansas (McKnight & Fischer, 1970) as but one example of many.

However, the Bisbee caves were strikingly different, and it would only become apparent by the late 1890s to those working in these mines that they were an oxidation feature. This concept was not originally agreed to and still is not universally accepted. This mechanism for cave development remains a controversial topic in the science of cave formation (speleogenesis), with many well-respected cave scientists somewhat skeptical of the position.

Douglas (1900) demonstrated the oxidation origin of these openings, and ever since economic geologists and miners, like ourselves, have long held the opinion that the caves in Bisbee formed in this manner. In 1927, the economic geologist, Edward Wisser, went to great lengths to convincingly demonstrate what others had long known regarding the formation of these caves. The authors are convinced that the origin of these caves is absolutely a function of the **complete**, near-surface oxidation of the carbonate-hosted, sulfide replacement deposits. As the genesis of these caves is totally dependent on the complete oxidation of sulfide mineral deposits, the term "oxidation cave" is used to describe these openings. This was accompanied by volume reduction, often substantial, through the removal of all of the sulfur and much of the iron. Other, more typical cave forming mechanisms, such as host rock removal by mildly acidic waters of meteoric origin, played a minor, if any, role in the development of this type of opening. Oxidation caves, as found at Bisbee, are typically isolated, single-chamber caves and cave-like openings, which are not connected or related to the hydraulic regimen. Oxidation caves occurred above large bodies of thoroughly oxidized iron oxides, clays/claylike minerals, and copper ore. Caves were also found above huge masses of iron oxides, with little if any copper ore present and, one instance, oxidized lead ores. This is a reflection of the original, largely pyrite, mineralogy of the sulfide masses before oxidation.



Sulfide replacement deposit at depth
Mineralogy: primary sulfides including pyrite, chalcopyrite, bornite

Partially oxidized deposit
Mineralogy: secondary copper and iron carbonates/oxides; azurite, malachite, cuprite, siderite, goethite, hematite with residual primary sulfides; pyrite, chalcopyrite, bornite and secondary copper sulfides; chalcocite, covellite

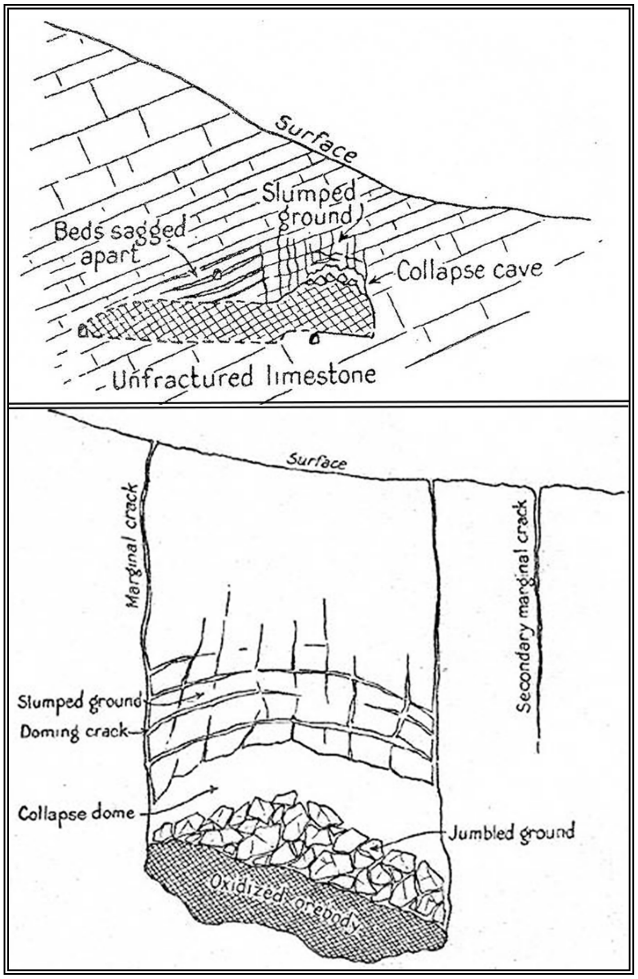
Totally oxidized deposit below oxidation cave
Mineralogy; secondary copper carbonates and oxides; malachite, azurite, cuprite, copper; in iron oxides; goethite, hematite; all with abundant calcite. Minor residual siderite.

Schematic representation of the development of an oxidation cave, beginning with the carbonate hosted, sulfide replacement deposit, passing into a deposit undergoing supergene alteration, then the fully developed cave with its impacts on the surrounding rock, compensating for the removal of support. Drawings by D. L. Graeme

The end result of complete oxidation is the substantially reduced volume of primary sulfides through complete sulfur removal as well as some of the iron, an enlarged, open area overlying and/or partially filled by the relatively small amount of remaining material. Recalling that the replacement deposits were primarily pyrite, usually, several times the volume of the copper minerals, which is totally oxidized, is why the remaining materials are characterized as a "relatively small amount."

The full and complete oxidation of the sulfide body is a necessary criterion for oxidation cave development. Siderite boxwork development was an intermediate step in oxidation cave formation. Ultimately, this siderite was altered to goethite by further exposure to acidic solutions as oxidation continued to generate acid (Trischka et al., 1929).

The goethite generated by the complete oxidation of the sulfide body was often tens of meters thick, soft, clay-like, and too weak to support itself and the rock above. Compaction of the oxidized ore body and collapse of the open boxwork structures in the lower areas effectively transferred these open spaces towards the top. The collapse of the boxworks and compaction of the supergene altered rock and clays destabilized the host limestone above the oxides by removing support.



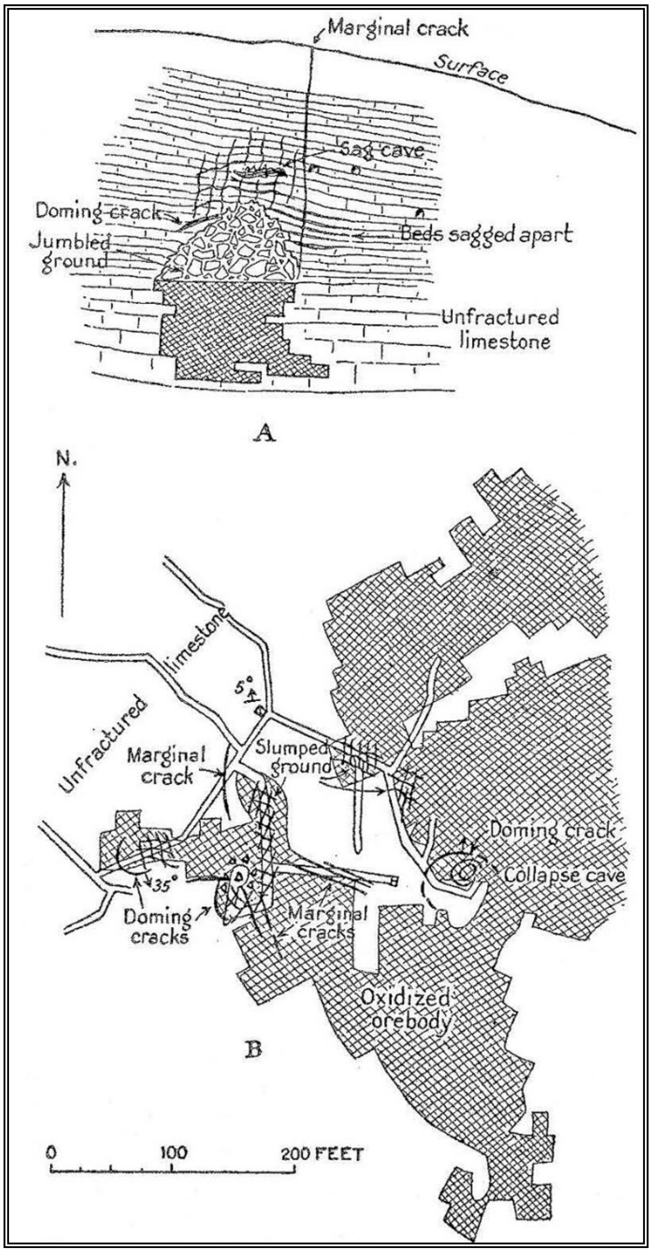
The overlying limestones characteristically responded to this lack of support by a partial or total collapse and/or subsiding as well as dilation of the limestone beds, creating open spaces and oxidation cave development. Subsidence occurred gradually as the supporting minerals were removed. When the host rock was sufficiently competent to develop a dome, a cave was formed. This was true for the upper Martin and all of the Escabrosa and Naco limestones, as illustrated to the left, from Wisser (1927).

Less competent units, such as the Abrigo and shaly lower Martin unit that cannot support an opening, tended to collapse and fill the resultant space with jumbled, typically sub-angular material.

Left: Features typically found with an oxidation cave development in thick bedded, competent limestone: notably the oxidized orebody below the cave, marginal cracks, sag caves, slumped ground, doming cracks and breakdown (jumbled ground). After Wisser (1927).

The separation of the overlying, host rock beds developed openings as they sagged due to the removal of support during oxidation of the sulfide bodies. These, too, helped create the principal void through collapse and/or developed secondary voids or "sag caves." Combinations of all of these features were common above thoroughly oxidized orebodies. Breakdown, the preferred term today, or jumbled ground as Wisser (1927) called it, was an important secondary mechanism for oxidation cave formation.

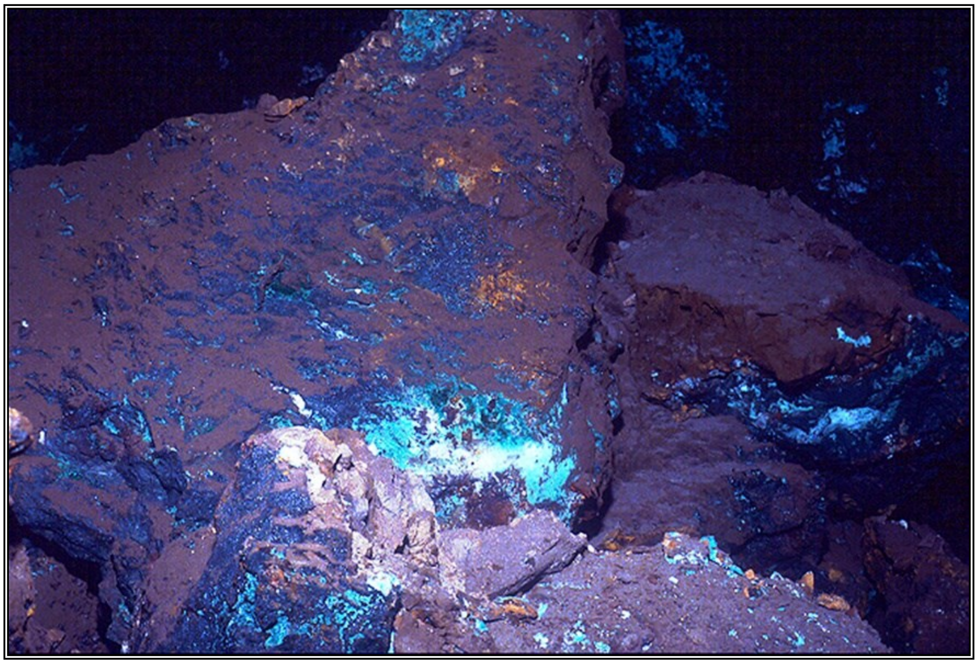
Consequently, boulders of the host limestone, often partially altered by supergene activity, were typically abundant in the cave bottoms, as were boulders of goethite and hematite, all having fallen from the walls and ceiling of the cave during development. Occasionally, chunks of ore minerals, such as malachite, were in the breakdown rubble. An example is illustrated below, where fresh limestone and chunks of malachite and goethite are cemented by calcite.



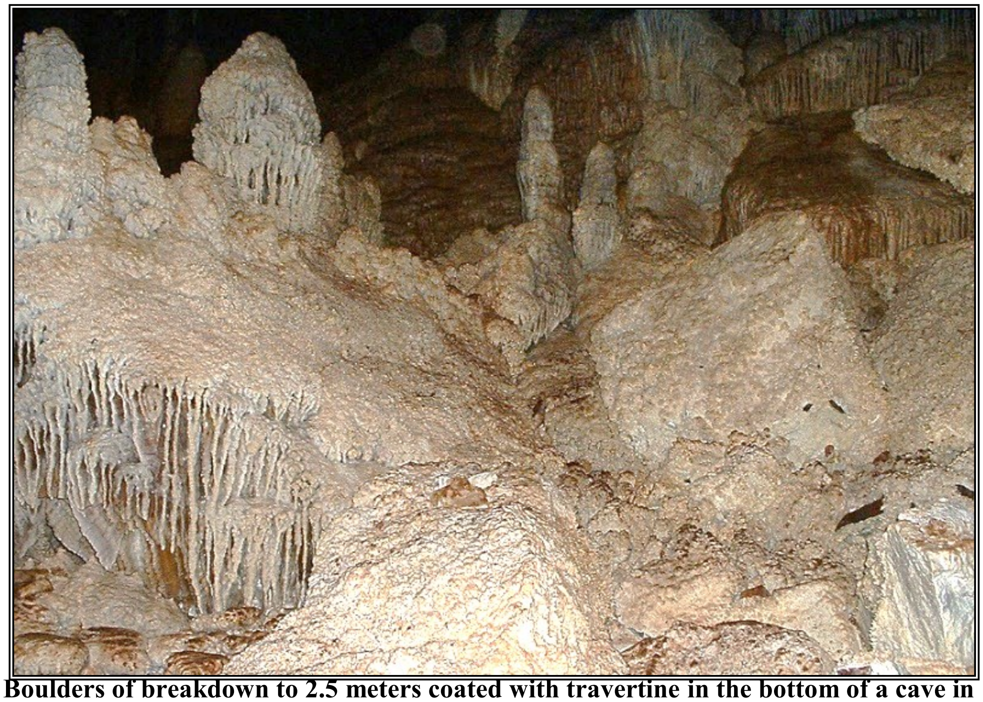
Features typical of oxidation caused collapse of thin-bedded, incompetent limestone. Note that the collapse area is small compared to the size of the orebody, but that several independent areas were impacted. After Wisser (1927)

Chunks of malachite with unaltered limestone fragments and goethite, all cemented together with calcite from a cave floor. These represent breakdown materials that fell from the cave ceiling or walls. 100 level, Holbrook Mine, specimen – 60 centimeters wide. Graeme collection

All of these materials had fallen from the cave ceiling or walls as a part of the breakdown process during cave development and are now cemented by calcite. The depth of the rubble often exceeded several meters in the larger openings. Indeed, boulders of several meters were a typical feature of large openings. In many of the caves, later, thick travertine deposition frequently obscured the breakdown deposit in the cave bottoms.



Breakdown composed mostly of hematite and goethite containing large amounts of rosasite as well as some malachite, "B" level, Uncle Sam Mine, view – 3.2 meters. Graeme/Larkin collection



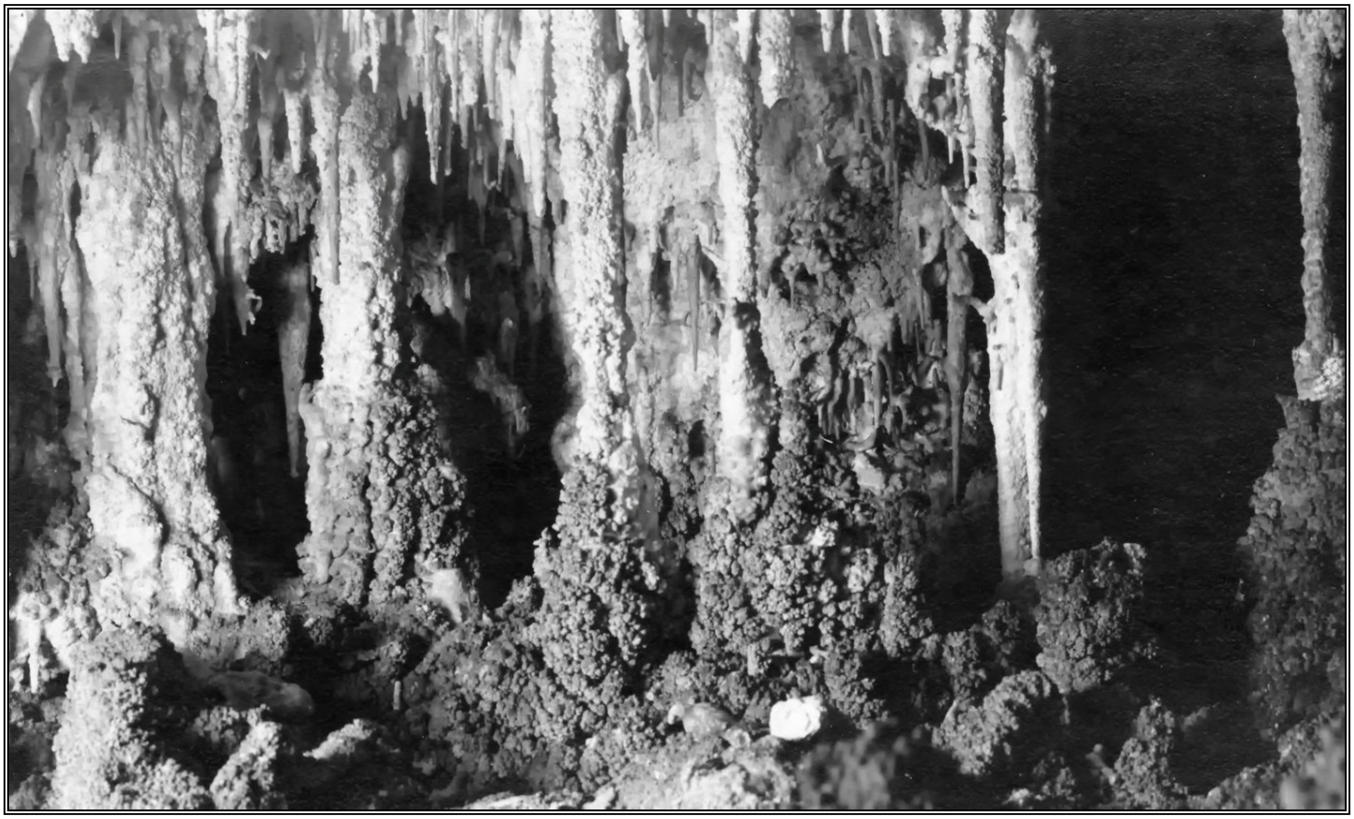
Boulders of breakdown to 2.5 meters coated with travertine in the bottom of a cave in the Southwest Mine 7th level. View – 7.7 meters. Graeme/Larkin collection

Beneath the breakdown and in the oxidation-generated iron oxides were abundant supergene copper minerals. Malachite and azurite were the most common and occurred as large masses and linings in the voids between boulders or lining the surviving goethite boxwork. On rare occasions, the rubble in the cave bottom was composed mainly of goethite with malachite and azurite, often in large pieces and little to no limestone present. These occurrences were extraordinary and the sources of incredible mineral specimens. Obviously, these areas were rich ore deposits as well. In a few, rare instances the cave bottoms were not mined because of low volume. The authors have found abundant, late-stage, supergene, copper minerals, including boulders of spongy malachite approaching a meter in an un-mined cave bottom.

One of the authors (RWG IV) with a 20-kilogram boulder of malachite found in the breakdown of a cave floor, 100 level, Holbrook Mine. Graeme/Larkin collection

The second type of cave formed by oxidation was what the miners referred to as "sag caves." Wisser (1927) also employed this appropriate term. These openings formed along bedding planes in the limestone above and adjacent to the oxidation caves.

As the support below was removed by oxidation subsidence, these openings developed through the dilation of the beds. It was uncommon for these types of caves to contain either iron oxides or ore minerals as they were well above the orebody. Also, the caves formed by dilation were typically small. Usually, the dilation of the beds did not exceed two meters in height. However, they could be up to 20 meters in length. All of these features are illustrated in the schematic, which illustrates the stages in the development of an oxidation cave over an orebody as it progressively oxidizes and the formation of sag caves in the overlying limestones.



Sag cave in the Holbrook Mine, circa–1905. View dimensions are unknown, but the vertical is almost certainly less than 1.5 meters. Graeme/Larkin collection.

Cross sectional view of breakdown in a cave bottom of altered Martin limestone blocks with some hematite, all cemented by calcite and resting on oxide ores of goethite with malachite. The ore had been mined, leaving only a small amount next to the oxidized breakdown, 100 level, Higgins Mine, horizontal view - 2.7 meters. Graeme/Larkin collection.

Nest of helictitic calcite in a sage cave that has collapsed into the oxidation cave below, 7th level Southwest Mine. Vertical view-1.5 m. Graeme/Larkin collection

OXIDATION CAVE FEATURES:

There are several characteristics common to all oxidation caves studied. These features are:

- Direct association with large amounts of sulfide oxidation products such as supergene goethite and hematite and secondary copper minerals
- They are isolated. The single-chamber features are not connected to or related to other caves and are not related to the current hydraulic regime, except that all are above the water table at the time of Bisbee's discovery
- All are relatively close to the current surface and in the western part of the district only, which is where four episodes of supergene activity occurred
- Subsidence-related cracks along the margins of the oxidation cave extended vertically for great distances, even to the surface where more-or-less conical depressions formed.

The single most important feature is the association of oxidation caves with thoroughly oxidized mineral deposits. All oxidation caves occur above and/or partially within masses of typically mixed oxide minerals, the more common of which are goethite and hematite. At Bisbee, substantial amounts of copper ore minerals often occurred within the iron oxides associated with the oxidation caves. The oxide masses associated with these caves were usually quite large, often 30 meters or more in total thickness. The lower portions of the oxide mass beneath the cave were invariably quite compact as a result of the weight of the overlying material coupled with the soft, often earthy, and clay-like nature of these oxides. In the uppermost portions of the iron oxide mass, voids, including boxwork structures, did survive. These boxwork voids were often the depositional sites for malachite, azurite and, other copper minerals, as were the voids in the associated rubble pile formed in the cave bottom by boulders of oxide minerals and limestone derived from breakdown.

Oxidation caves are always very limited in extent, occurring as isolated, single-chamber openings whose size and shape was a direct function of the size, shape, and orientation of the original sulfide deposit as well as the nature of the host rock. In the very few caves where more than one chamber appeared to exist, it was typically an expression of localized breakdown accumulation nearly filling the opening; travertine or speleothem deposition forming a partition-like wall or by variable dilation along several bedding planes in the host rock.

Large orebodies frequently had more than one cave develop over the oxide ores. The large cave on the 300 level of the Shattuck Mine was, in reality, two oxidation caves that formed over the opposite extreme of a huge, mixed copper/lead orebody. The two caves were separate on the 200 level and above but merged on the 300 level, where both caves were at their largest.

All of the oxidation caves in Bisbee occur within 300 meters of the present surface. This is not too surprising since sulfide oxidation, which played a major role in forming these caves, is limited by the depth to which oxygen-rich water penetrates below the surface. Minor sulfide oxidation has been recognized at Bisbee to depths exceeding 800 meters along the major geologic structures, and intense oxidation was also common to a depth of 600 meters. This deeper supergene oxidation is largely an artifact of the first episode of activity that occurred during pre-Cretaceous times and is only so deep because of subsequent burial by Cretaceous sediments. Because the first phase of supergene activity did not totally oxidize the orebodies it affected, there are no oxidation caves associated with orebodies that experienced just this first phase of oxidation. There can be little doubt, however, that it did contribute to their development in the western part of the district. Oxidation caves are, without exception, restricted to the western part of the mineralized area, that portion of the district which experienced the four distinct phases of supergene activity. It was the last two phases of supergene activity that completed the oxidation of the orebodies and caused the formation of the caves. Thus, they are a late feature, if not very late.

While no dating tests have been made on speleothems from Bisbee, we believe these features to be very young. They appear to be no older than the late Pleistocene, more or less some ±300 kya. This supposition and, that is what it is, is based on comparison to other southwestern U.S. cave studies, paleoclimatic indicators, and the historic water tables, as indicated by supergene activities.

The marginal subsidence cracks are unique to oxidation caves and encircle the cave. These are, as the name suggests, cracks that form around the margins of the cave as the overlying limestone plug drops in response to the removal of support from below caused by oxidation shrinkage. This feature, alone, is proof that the caves did not exist before mineralization took place, or these cracks would have been conduits for hypogene mineralizing fluids. This was not the case, however. To be sure, supergene solutions followed these features.

Marginal cracks surrounded conical depressions. These were essential aids in prospecting. Wisser (1927) observed that marginal cracks were commonly lined with, if not entirely filled by travertine-type calcite, indicating openness to solution passage. An example is shown below.

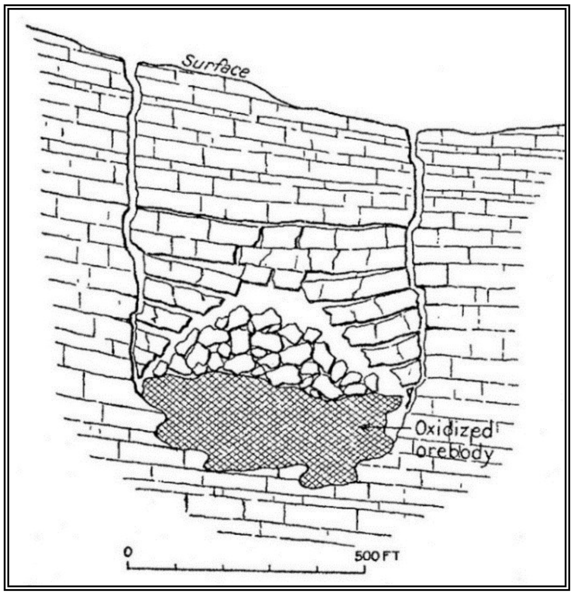


Diagram showing marginal crack along the cave boundaries (Wisser 1927).

One of the authors (RWG III) next to a calcite-filled marginal crack high on the east slope of Queen Hill. Graeme-Larkin collection.

Polished aragonite/calcite stalactite cross section showing the episodic nature of growth, which can be roughly correlated with speleothems from other regional caves as well as varying copper coloration and mineral inclusion during deposition, 4th level, Southwest Mine, specimen – 30 cm, 4th level Southwest mine. Graeme collection.

THE ABSENCE OF OTHER CAVE TYPES AT BISBEE:

The 25-kilometer-long Mule Mountain Range, in which Bisbee is situated, is, in large part, composed of limestone representing various Paleozoic and Cenozoic units. However, in spite of the abundance of limestone, there are but two known, small karst developed caves, both well outside the mineralized area and both in Naco Limestone. One lies 14 kilometers to the northwest of the city of Bisbee, while the other is just over ten kilometers due west.

Minor karstic enlargement of faults in the limestone is a common occurrence at Bisbee, as would be expected in this carbonate environment. However, this was highly localized in nature and never extensive or large. Miners referred to these openings as "watercourses" as they frequently would contain modest amounts of water when found. Most drained soon after being hit by mine workings and usually remained dry. In the mine workings nearest to the surface, rainwater would quickly flow from these openings following a significant rainfall event, but they would soon be dry again. There is no recognized connection between these openings and the oxidation cave development.

Within the five-kilometers by three-kilometers mineralized area, there is a total absence of non-oxidation-related caves. It would be reasonable to expect that if there were caves, they would have been found, given the immense amount of underground development (>3,500 kilometers of workings) and diamond drilling that took place (>4,000 kilometers of exploration drilling). A few small, post-ore, hydrothermal voids are known to have been hit during mining and exploration drilling. None were associated with the supergene activity. All were free of sulfides and barren, except for hydrothermal calcite, some with minor hydrotherman goethite and/or manganese oxides.

That the ores were not deposited in pre-existing caves or openings is also demonstrated by the fact that hundreds of ore bodies, both hypogene and supergene, were mined that were not associated with any type of opening, hydrothermal or supergene-developed.

There is a notable absence of sulfide mineral crystals at Bisbee. Large sulfide mineral crystals are a feature typical of sulfide deposits emplaced in preexisting voids. This lack of sulfide mineral crystals is true throughout the whole of the mineralized area.

In our view, all of these factors are further indications that the sulfides were not deposited in pre-existing open spaces and that there is little chance the caves

Calcite with a light coating of goethite lining a hydrothermally developed void, 2700 level, Campbell Mine. Photo taken in 1973. Graeme-Larkin collection

associated with the oxide ores were developed by mechanisms other than complete sulfide oxidation.

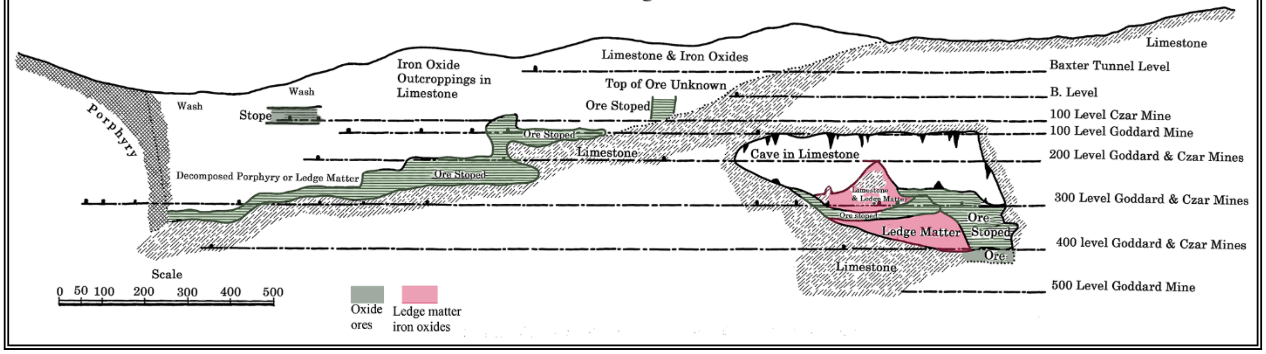
CAVE DEVELOPMENT FEATURES AS A PROSPECTING AID:

Given this strong correlation between oxidation of sulfide ores and subsidence with cave formation, a great deal of effort was spent looking for those cave-related features, which would indicate the possible presence of ore (Douglas, 1900, Wisser, 1927). Features such as caves, subsidence generated marginal cracks, doming cracks, sag caves and, the presence of limestone broken because of subsidence below were all indicators that suggested ore might be someplace below. Siderite or massive goethite, which had replaced siderite, would indicate to the miners that they must look upward in their search for ore.

In his paper, Dr. Douglas wrote:

> "*A feature of the Bisbee mine is the large caves, which had some influence on the occurrence of the oxidized ore bodies. The walls, roofs and floors of these caves are always covered with stalactitic accretions, which are often tinted green, blue and red by the copper and iron solutions which are mixed with a solution of lime. What, however, gives these caverns practical interest is that they have invariably covered oxidized ore bodies. Fig. 14* [shown below] *gives a cross-section through one of the large caves. Three such caves of considerable extent have been encountered, and in every instance this combination has occurred. It may be accidental; but so satisfied are we to the contrary that, when a cave is now met with, drifts are run beneath it to strike the ore body. It is a fair assumption that the cave, if not originally formed by the contraction of an ore-body, was increased by the shrinkage of the latter during its oxidation, and that, therefore, a genetic relation really exists between the cave and underlying ore*" (Douglas, 1900).

Fig. 14



A large, Martin limestone hosted cave (100 M X 170 M) in the Holbrook (Goddard) Mine, showing the restriction to limestone hosted ores and with oxide ore in the bottom along with supergene clays/iron oxides. After Douglas, (1900).

It was the success of using the oxidation cave features as a guide to ore that inspired Wisser (1927) to write his paper on these features. A good number of other limestone-hosted deeply oxidized ore deposits worldwide existed where this knowledge could be profitably applied. For Bisbee itself, this was common knowledge. The understanding of these features had been successfully used for decades, but sharing information was a hallmark of the Copper Queen

Consolidated Mining Co. No doubt, Wisser was encouraged to share this with all who could apply the information at their various mines around the world.

A crosscut driven through blocky, chaotic boulders of broken limestone showing dilation and breakage along bedding planes, subsequently cemented by minor calcite. A feature such as this was an important guide to possible ore somewhere below. This is 86 Crosscut on the 6th level of the Southwest Mine and mining through this broken rock would have been both difficult and dangerous as large blocks of limestone fell from the sides and back (top). Maximum width - 3.5 meters. Graeme/Larkin collection.

A typical, limestone crosscut in rock not impacted by cave development. The chute near the end suggest that ore was mined above, as some goethite was present in this small area. This location is on the same level and about 60 meters from the location illustrated to the left. Horizontal view-2.2 meters.

Fissure on the 200 level, Czar Mine (Douglas, 1900). This was undoubtedly a subsidence caused, marginal crack.

Minor botryoidal calcite growth along a doming crack above an oxidation cave, "A" level, Copper Queen Mine, 1967. Graeme/Larkin collection. Al Voirin, miner and collector of note is in the photograph.

A LOOK AT TWO OXIDATION CAVES:

While oxidation caves have a good number of common features, each one had individual differences. The hosting limestone responded somewhat differently to the mineralizing fluids with the Martin limestone hosting, tabular, manto-type deposits. The mineralization in the Escabrosa and Naco units were typically more chimney-like. The resultant oxidation caves retained these features. The Abrigo, a thin-bedded and shaly limestone, was incompetent and collapsed when completely oxidized ores were below.

Multi-phase hypogene mineralization was quite variable in the replacement deposits. A greater pyrite content in a replacement deposit would develop into a relatively larger cave than a high copper mineral one. While generally modest, the variable chemistry of the hypogene ores would result in different secondary accessory minerals, some of which were found at their best in these caves. Below is a brief overview of two oxidation caves and their features.

The above photo of an oxidation cave was taken by Pete Kresan with us in 1973. It was found during mining in 1926 and was to be the last cave of any size to be discovered. It was also the west-most oxidation cave ever found at Bisbee. It was located some 25 meters above the 7th level of the Southwest Mine, at about 1, 760 meters AMSL making it the highest in terms of elevation as well.

Because it was near the sideline with the Higgins Mine property and access was much easier through the portal of the Higgins Mine, it soon became known as the "Higgins Cave" even though it was actually located within the connected Southwest Mine. It is some 80+ meters long, by 30-40 meters wide, and up to 15 meters high. Its tabular form is typical of Martin limestone-hosted oxidation caves reflecting the general manto form of the original sulfide replacement deposit. Numerous sag caves were found above, as were doming cracks. Both opening types were often well decorated.

This was a magnificent cave by any standards. It was highly decorated with spectacular stalactites and huge stalagmites. Interestingly, stalagmites were uncommon in Bisbee's caves, as the cave bottoms were unstable and always moving downward as oxidation and compaction continued. Nearly all of the hosting rock in the cave walls was coated by strikingly beautiful speleothems, including numerous, large nest of helictites and extraordinary colorless to white jackstraw clusters of aragonite with crystals to five cm.

This cave was one of the few which contained a small pool of water. It seemed to be at equilibrium with the inflow from dripping stalactites and evaporation.

As was typical, the cave had developed over a copper orebody. This one contained some ± 25,000 tonnes, extending below the 7th level. The stope walls were uncommonly dry and stable, leaving colorful, massive hematite and goethite following mining. No backfilling (gobbing) took place above the 7th level as there were no workings above to provide fill material.
Like many other oxidation caves, it was partially within massive iron oxides.

Massive, supergene hematite in the back and deeply hematitic colored speleothems at the left. 7th level, Southwest Mine. P. Kresan photo, 1973.

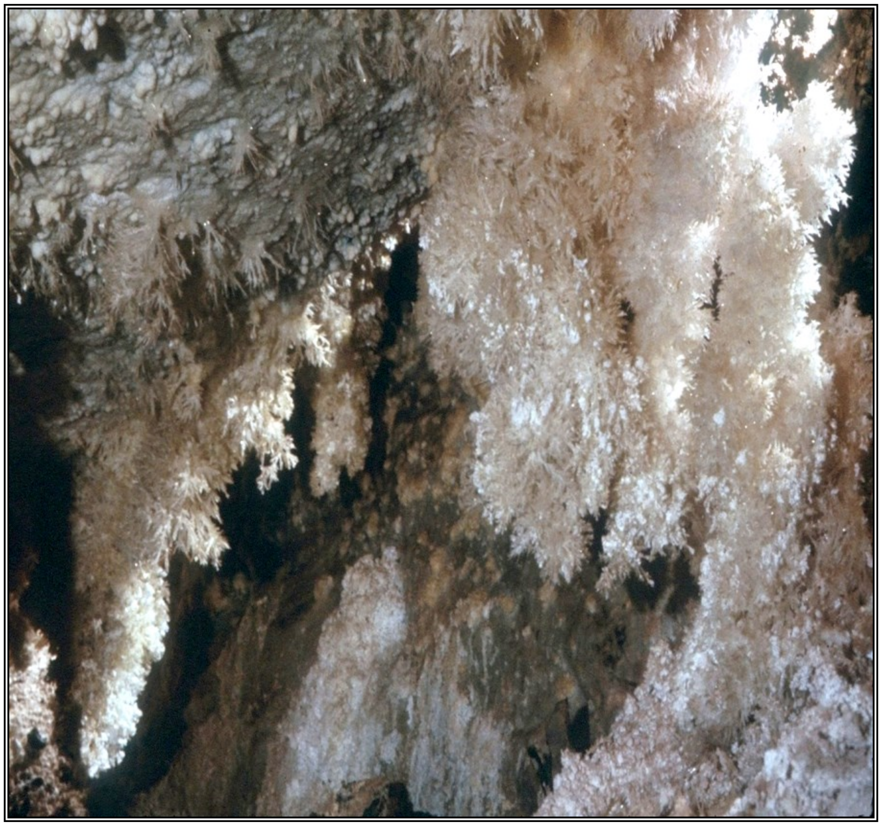
Speleothem coloration was far less common in this cave than most. Locally, iron coloration was intense. The cave was less than 30 meters below the surface, which allowed for humic coloration in some small areas. Both iron and humic coloration can be seen in the photo to the left.

As this cave was well above any copper mineralization, tinting by Cu was limited to a tiny area of aragonite. Near this same area were patches of lightly green tinted calcite, with the color coming from overgrown and included conichalcite, something not seen elsewhere. Small crystals of yellow/green mottramite with aragonite and calcite were abundant in one area. Exceptional, splendent plattnerite crystals to two mm, in radiating clusters, occurred on altered limestone, as shown below. Also found nearby were small bright yellow pyromorphite crystals.

A close up of the below aragonite. View-18 cm.

Plattnerite, as splendent crystals to 4 mm on altered limestone, 7th level, Southwest Mine, View-1.6 cm., Graeme collection.

Right: Aragonite, in stalactite-like forms to 45 cm, on calcite with minor white dolomite. The masses are jack-straw clusters of two to five cm, white to colorless aragonite crystals. These formed in a doming crack associated with the above discussed cave, 7th level, Southwest Mine. Horizontal view-1.2 m. Graeme/Larkin collection.



A classic oxidati0on cave on the 100 level of the Holbrook Mine. Author DLG is seated on the stalagmite some 45 meters above the cave floor. Graeme/Larkin collection

This chimney-like oxidation cave to the left reflects the general shape of the sulfide replacement deposits in the Escabrosa limestone, which were chimneys. The orebody under this cave was mined on the 100 level of the Holbrook Mine, and well under Queen Hill, sometime during the 1890s. Fortunately, the cave was left unmolested for three-quarters of a century, as access from the Holbrook was long caved and only recovered in 1972 with the Lavender Pit expansion.

The person sitting on the stalagmite is already 45 meters above the cave floor. The overall height of ± 70 meters brought the top well above the collar elevation of the Holbrook shaft as it was well under the high Queen Hill.

It was a truly lovely cave; large parts of the walls coated with sparkly malachite. Impossibly high on the wall was an enormous void with malachite stalactites reaching 50 cm.

Meter plus masses of chrysocolla, suggesting coated cuprite boulders, were seen in several places. Speleothems in all forms ranged from white to multi-tones of green to aqua blue.

Iron had colored large areas of calcite deep red/brown. At some point in time, the lower two meters had flooded, with light-brown, elongated calcite rhombs to 15 cm, recording this phase.

The breakdown was uneven, forming a high shelf from which the accompanying photograph was taken. Masses of spongy malachite, which had fallen from the walls in meter-sized masses, were found mixed in the breakdown.

In addition to the minerals noted above, splendent two-three cm crystals of plattnerite were common near the bottom, both on and included in colorless calcite. Rosasite with tiny hemimorphite crystals was abundant on the lower east side of this cave.

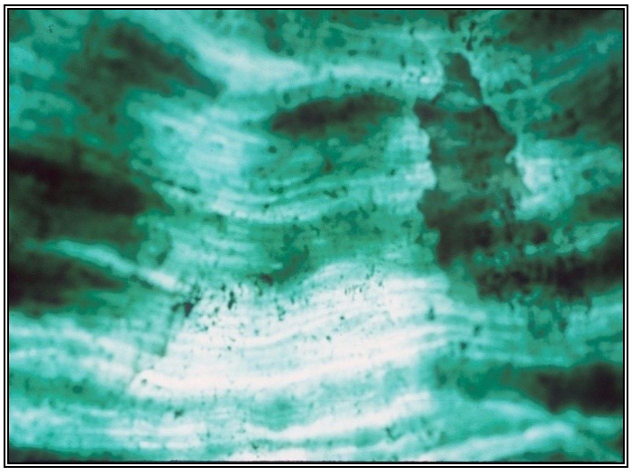
Top-left: a four-meter view of a wall section with a coating of malachite and chrysocolla to several centimeters thick, partially overgrown by white and red calcite.
Top-right: Several helictic nests of lightly-blue tinted aragonite are in the center of the photograph. Both of the larger groups exceed 50 cm in size and stunning to look at. Graeme/Larkin collection
Right: One of the authors (DLG) exploring the extent of a boulder of malachite in the oxide ore on the cave wall very near the cave bottom. Malachite was abundant as irregular masses in the iron oxides. For the most part, it was spongy in texture and not interesting at all from a specimen perspective.

SPELEOTHEM COLORATION:

Multi-colored calcite/aragonite stalactite section showing the green copper coloration of calcite, red of iron in calcite as well as the blue-green color imparted by copper to aragonite, at the right. Czar Mine, specimen-17 centimeters. USNMNH specimen.

As has been noted above, it was common for speleothems in the oxidation caves at Bisbee to be colored, often intensely so. The stunning effect that copper frequently imparted to the coloration of these caves defies description. Much of the coloring by copper and iron was transported in the solutions from mineralized areas above the cave, with only minor amounts coming from the cave walls. Consequently, the caves that were in the highest positions with little, if any, mineralization above were typically less colorful than those lower in the system.

Copper tinted both calcite and aragonite speleothems. This coloration was often two-fold in origin: substitution of copper for calcium on an atomic level and/or simultaneous deposition of malachite with the calcite or aragonite. Azurite has never been noted as inclusion or colorant in calcite or aragonite. This is, no doubt, due to the pH as the pH range for azurite formation is lower than that of aragonite and calcite.



Polished section of a calcite stalactite, showing calcite co-deposited with malachite as flecks to 0.5 millimeter imparting a strong green tint, Czar Mine, view–8 cm

Substitution of calcium by copper on an atomic level produced a green tint in calcite and an aqua hue in aragonite. The degree of coloration in speleothem of either mineral was quite variable, ranging everywhere from just a slight tint to medium green for calcite or aqua for aragonite. However, the mineral remained calcite or aragonite. A good discussion of the substitution mechanism for coloration can be found in White (1981 and 1997).

The simultaneous deposition of malachite occurring along with the deposition of calcite or aragonite, while far less common, was not rare. The malachite deposition was not constant but rather interspersed with periods of normal color calcite deposition. This suggests an extension of the copper source or a change in the solution flow path.

Iron-colored speleothems are most often developed from staining and co-deposition of goethite from moderate pH, iron-rich solutions flowing down the cave wall. Tiny specks of goethite or hematite are often included, and some surface corrosion is common.

Aragonite on calcite. The aragonite crystals are partially tinted by included tiny specs of goethite, 3rd level, Southwest Mine, view – 9 cm. Graeme collection.

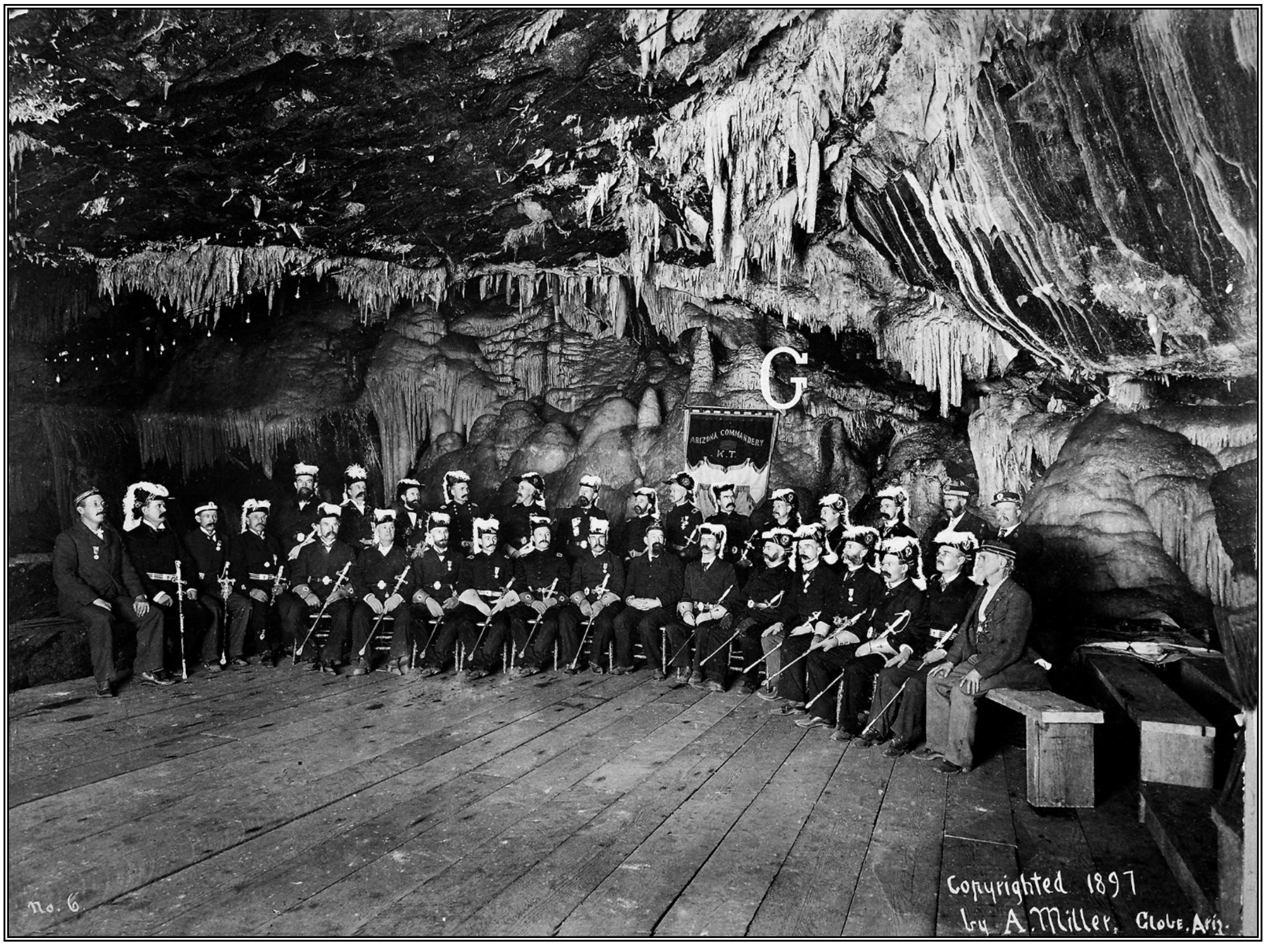
Few Bisbee caves were very close to the surface, with most exceeding 50 meters below the current surface. Fewer yet had the type of hydraulic connections to the surface as seen in karst caves, so few contained speleothems colored by organic substances, i.e., humic substances.

Calcite flowstone, colored by humic acid, engulfing stalagmites, 7th level, Southwest Mine, horizontal view - 3.2 meters. This area is less than 30 meters from the surface. Graeme/Larkin collection.

The incorporation of humic acids derived from overlying soils is recognized as the cause of the various shades of speleothems coloration, from red/brown through orange and white. For most such speleothems, the color is due to higher molecular weight humic substances incorporated in the calcite crystal structure (Brennan & White, 2013).

Right: Calcite and aragonite stalactite showing coloration by copper and iron caused by co-deposition. In the case of iron, goethite was deposited as micro flecks on the surfaces as the stalactite grew and were included in the calcite with some corrosion. Copper coloration is the result of tiny particles of malachite deposited simultaneously with the calcite as well as some substitution of Cu for Ca. As can be seen, there were periods of calcite deposition without any coloration, 4th level, Southwest Mine, view - 8.2 centimeters. Graeme collection.

VISITORS TO THE CAVES:



Meeting of the officers of the Arizona Grand Lodge of the Masons in the Copper Queen Cave on the 200 level of the Czar Mine, November 10, 1897. Graeme/Larkin collection.

Even though these caves were common at the time, their splendor was always appreciated by all who saw them; miners and visitors alike. From the earliest of times, the Copper Queen Consolidated Mining Co. (Copper Queen) allowed ready access to its mines so that all who wished could visit the caves as they were found. The Shattuck and Arizona Mining Company, a smaller operator nearby, also extended the same courtesy to the interested public. This most enlightened policy, which allowed literally hundreds to see the beauty hidden in the barren, limestone hills. More than a few special events were hosted in a special such opening. The most noted was the 1897 meeting of the Masonic Grand Lodge of Arizona, which was held in a spectacular cave on the 200 level of the Czar Mine. Some 50 plus Masons from around Arizona and several other states and territories were in attendance. The Arizona Elks held their annual meeting in Bisbee in early April 1916. The highlight of this gathering was a luncheon and a dance held on Saturday, April 9th, in the Shattuck Cave.

Occasionally, the splendor of a cave was recorded by written descriptions or photographers who visited. As was often noted by the authors, it was impossible to adequately describe the wonder of these caves with words or black and white photographs, but they attempted to do so as best they could.

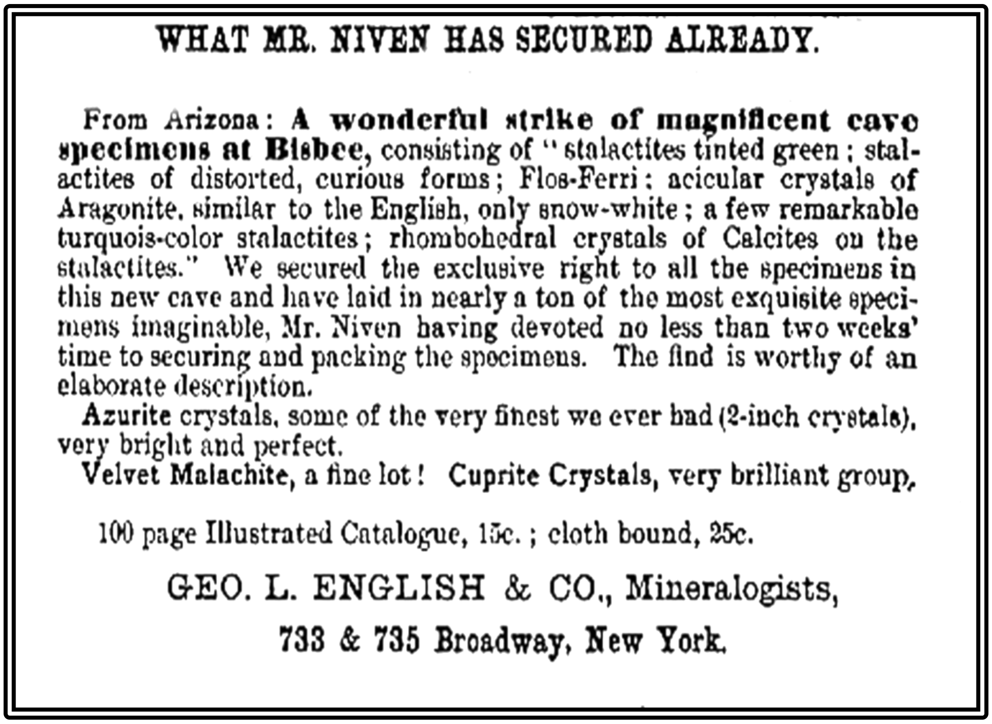
Among those who attempted this near-impossible task was William Niven. Prominent New York mineral dealer George English had sent William Niven to Bisbee in 1890 to acquire minerals for resale. With the assistance of the Copper Queen, Niven recovered a ton of specimens from a cave in the Czar Mine beneath Queen Hill. In doing so, he gave us the earliest detailed description of one of Bisbee's oxidation caves. An excerpt from a letter he had sent to English was published in the July 1891 issue of *Mineralogist's Monthly* and offered the following:

> "*It is 80 feet wide at the mouth, 270 feet wide about the center and 250 feet wide at the end, and is 500 feet in length. From the mouth of the cave to the end it is at least 150 feet high. There are four chambers, each of which has its own peculiar habit of crystal form. In No. 1 are to be found the acicular crystals of aragonite. No. 2 consists mainly of flos ferri. No. 3 is the grandest of all, and looks like a magnificent cathedral-most of the stalactites and stalagmites are colored green with the copper, and they look like immense organs, while hanging from the roof is a bunch of stalactites which looks like a gigantic chandelier. In some places the form is like roses, again like fringe, coral, palm leaves, trees, toadstools; in others great slopes of glaciers and fields of ice. . .. In one place more is a great number of sheets of aragonite from 3 to 4 feet long and 2 to 3 feet wide, about 1/2 to 3/4 inch thick, beautifully translucent, showing alternate layers of green, white and blue and resembling tapestry when a light is placed behind it. . .. I spent 14 days in this vast cavern. While I was selecting specimens, I had a photographer take pictures; you can imagine the singular scene the main chamber presented with 200 candles burning. It was a scene of dazzling beauty. Countless stalactites of every conceivable shade of green, blue, red-intermingled by snow-white, hanging from the roof and sides-while rising from the ground great ghost-like stalagmites stood silent sentinels guarding this incomparable workshop of nature's laboratory*."

Why? One would reasonably ask, was this obvious vandalism allowed. In truth, this was a salvage effort; one that had happened before and would be repeated many times over the next 40 years. Under most any other circumstances, it would have been absolutely inappropriate to remove formations from these caves, much less completely ruin them. This collecting was truly salvaging.

Salvage, because these wonderful caves were victims of their genesis. The rich ores below and within were to be mined and, by necessity, the cave backfilled for safety reasons. The colorful stalactites and other cave formations were collected by the mining companies, the miners themselves, museums, and mineral dealers to save a bit of the magnificence soon to be lost. These remain today as a feeble geologic artifact of nature at its most beautiful.

For a number of reasons, above all, safety, these caves were destroyed. Essentially the caves were mined because the great majority either contained or occurred above substantial amounts of ore. Had the ore not been mined and left in place to preserve even one cave, the costs in both economic and social terms would have been enormous, indeed, unacceptably high. And too, this would have created a potential safety hazard.



WHAT MR. NIVEN HAS SECURED ALREADY.

From Arizona: **A wonderful strike of magnificent cave specimens at Bisbee,** consisting of "stalactites tinted green; stalactites of distorted, curious forms; Flos-Ferri: acicular crystals of Aragonite, similar to the English, only snow-white; a few remarkable turquois-color stalactites; rhombohedral crystals of Calcites on the stalactites." We secured the exclusive right to all the specimens in this new cave and have laid in nearly a ton of the most exquisite specimens imaginable, Mr. Niven having devoted no less than two weeks' time to securing and packing the specimens. The find is worthy of an elaborate description.

Azurite crystals, some of the very finest we ever had (2-inch crystals), very bright and perfect.

Velvet Malachite, a fine lot! **Cuprite Crystals,** very brilliant group.

100 page Illustrated Catalogue, 15c.; cloth bound, 25c.

GEO. L. ENGLISH & CO., Mineralogists,

733 & 735 Broadway, New York.

Ad for these specimens collected by Niven from an 1891 issue *of The American Journal of Science*.

The obvious loss of revenue from the large amounts of ore found, yet not mined to preserve a single cave, may have placed the mine in an economically precarious position. Men may have lost their jobs. This would have had huge economic repercussions well beyond Bisbee. The Copper Queen Mine was the economic engine of southern Arizona at the time.

Also, the high costs associated with maintaining access to the cave would have been unsustainable. Maintaining safe access through the mine shafts and other openings (crosscuts) in these soft ore areas where the caves occurred would have been both difficult and inordinately expensive. Huge amounts of support timber and constant maintenance would have been required. For example, 30 board feet of support timber was required for every ton of ore removed from the mine, and this was just to keep the mine workings open on a short-term basis while the ore was being extracted, as noted by the Bisbee Daily Review, (1904).

> *"The ore bodies are so soft that the problem of timbering is a serious one, the mine requiring about thirty feet of timber, board measure, for every ton of ore taken out, and it is frequently necessary to bulkhead the openings to them to keep them intact. The whole mountain under which the mines are opened, seem*[sic] *to be creeping, but despite the threatening circumstances under which the ore is taken, the exceeding care exercised in timbering, renders the mine safe, and great accidents due to the caving in of the ground have never occurred."*

During mining operations, oxidation caves presented a very real and significant hazard. In unstable rock conditions, such as those found at Bisbee, all openings of any size must be backfilled (tightly filled with mined waste rock) to prevent the movement and collapse of the ground (rock). Such rock movement could dangerously affect nearby areas.

Also, as these caves formed, natural subsidence occurred in and around the cave leaving the host rock relatively weak and largely unstable. This pervasive fracturing was clearly illustrated by Wisser (1927). He further notes that the effects of subsidence extended as much as 300 meters above the oxide orebodies and associated cave, fracturing the rock hosting the cave, making the surrounding area unstable and complicated to mine.

For these reasons, the cave areas were mined, and the remaining openings backfilled as completely as possible. Today, the only records that remain of these caves include the awe-inspired descriptions written by those fortunate enough to see them; historical photographs, mostly in black and white, and the many specimens recovered before the caves were lost during mining.

A view of Queen Hill from the top of Sacramento Hill, circa 1918. Crossing the center of the photo are wide, deep subsidence cracks with up to 10 meters of vertical displacement and 5 meters of horizontal displacement. Vertical cracks, while less obvious, can be seen in the face of Queen Hill directly above the city. A massive rotational failure has encompassed most of the face above Bisbee.

This was a constant source of concern for all and every effort possibly made to halt this potentially catastrophic collapse was taken. Most importantly the tight backfilling of all open spaces, including the many caves. By the late 1930s, the movement slowed and eventually stopped, as mining of the area ended.

TURQUOISE, A NEW BISBEE CLASSIC:

A BRIEF HISTORY:

When turquoise was first found in the Lavender Pit and became important to Bisbee is uncertain, but it was in the early- to mid-1950s. The myth that Bisbee turquoise was incorporated in native American jewelry prior to this time is just that - a myth. As for local mineral collectors, the strong engrained collecting culture at Bisbee was not interested. We had long focused on the copper carbonates and the other crystallized minerals for which Bisbee is so noted. This new stuff, blue streaks in a red/brown rock, did little to inspire the many collectors in town, and there were few lapidaries in Bisbee to get excited. There is no record of when Bisbee's turquoise began its climb to fame, but by 1960 Phelps Dodge (PD) had continued with its long history of assuring that minerals were recovered and saved in a safe and reasonable manner. To maintain the policy of saving important minerals, while ensuring employee safety, an exclusive contract for turquoise recovery was awarded to Bisbee Blue® Mining Co., owned by Bob Mathews.

Unlike the underground mines, the open pit presented a number of very real safety concerns, which precluded the casual collecting by the employees in the pit. The operators of the huge equipment – 65-ton capacity trucks and electric shovels - could not see anyone close by on the ground and, a considerable risk that could be addressed only by keeping the workers in their equipment. And too, the Glance Conglomerate, which was the only rock type that hosted turquoise, was unstable, dangerously so. The 15-meter-high rock benches would suddenly collapse with little to no warning; anyone close to the toe (bottom) was very much at risk.

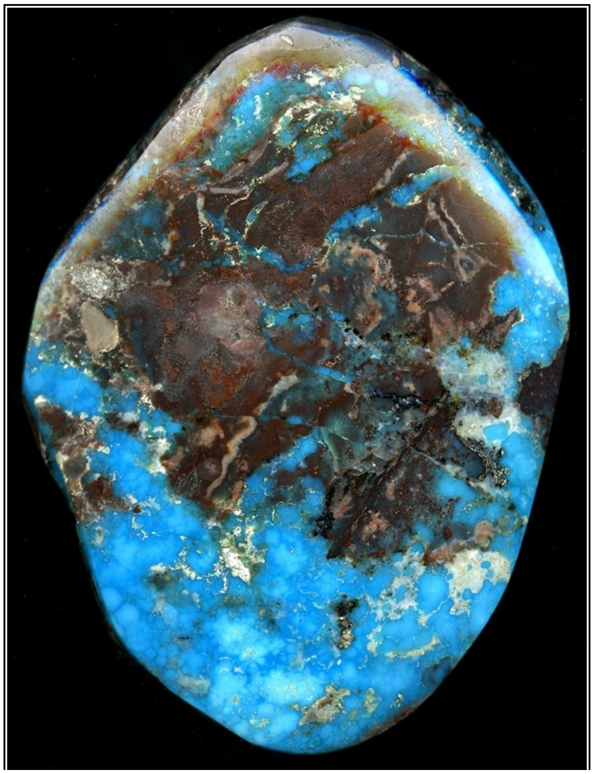
For Bisbee, the turquoise recovery contract was a win-win; the material was saved by a competent miner who was also a savvy marketer. To be sure, a good deal of turquoise was still surreptitiously collected by the truck drivers, shovel, and bulldozer operators, but this was now a dischargeable offense for reasonable safety reasons. Unfortunately, more than a few men became ex-employees of PD for collecting this blue rock while on the job.

The hosting Glance conglomerate contained no ore, so it was sent to the #7 waste dump east of the pit, first by train and then later by newer 65-ton haulage trucks. Some local residents would climb the 70-meter-high dump at night to search where promising material had been dumped. As the haulage units dumped over the dump edge, a very real danger presented itself with boulders rolling down the slope with each tipping of a railcar or haul truck. Security to protect fools from themselves was put in place, but the turquoise diggers worked with flashlights under blankets to hide their presence.

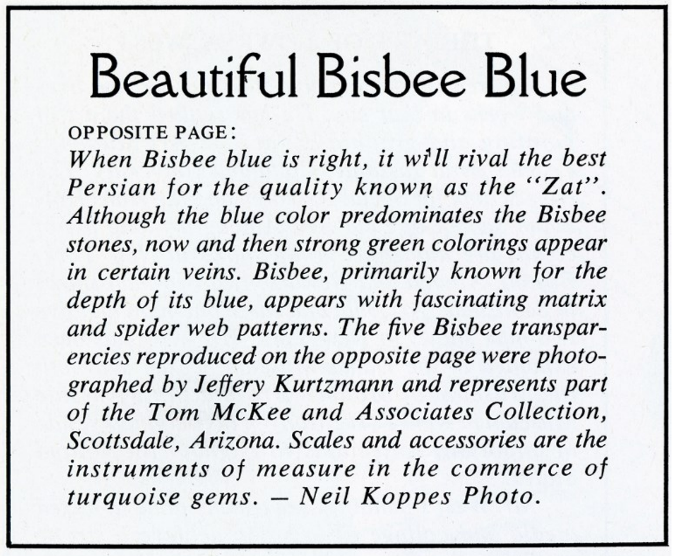
This illicit turquoise collecting continued off and on for more than 40 years after the mine closed, obviously with diminishing returns. In no way did the Mathews recovery contract have any significant positive financial impact for the mining company, but it may well have prevented horrible accidents, which were the real concerns for PD.

Today, Bisbee's fame for its extraordinarily fine turquoise matches that of its fabulous azurite and malachite specimens. A discussion one of the authors had at the Tucson Gem and Mineral Show in 1967 with Paul E. Desautels, a mineralogist, and at the time, curator of the Department of Gems and Minerals, at the National Museum of Natural History (Smithsonian Institution) put Bisbee's turquoise in clear perspective. He said the "the very best Bisbee turquoise was as good as, or better than the best from any other locality in the world." Paul, now paraphrasing, also said that just before coming to Arizona, he had reacquainted himself with all of the turquoises in the museum collection because of the strong interest he would encounter.

Paul must have said something similar to others, or others shared his opinion. Below is an insert from the January 1974 issue of *Arizona Highways* magazine. The article by Neumann (1974) that had this insert noted that Bisbee began producing excellent turquoise in 1967.



Turquoise with fragments of Glance conglomerate. The 8 mm thick piece has been cut and polished, but is otherwise untreated. Lavender Pit Mine, specimen-5 X 6.5 cm. Graeme collection.



Beautiful Bisbee Blue

OPPOSITE PAGE:

When Bisbee blue is right, it will rival the best Persian for the quality known as the "Zat". Although the blue color predominates the Bisbee stones, now and then strong green colorings appear in certain veins. Bisbee, primarily known for the depth of its blue, appears with fascinating matrix and spider web patterns. The five Bisbee transparencies reproduced on the opposite page were photographed by Jeffery Kurtzmann and represents part of the Tom McKee and Associates Collection, Scottsdale, Arizona. Scales and accessories are the instruments of measure in the commerce of turquoise gems. — Neil Koppes Photo.

To be sure, the "best" is a very subjective appraisal, so it must be considered in the context of what he was comparing, but this was the opinion of a knowledgeable and neutral observer. It was at the height of the turquoise craze, with unreal prices being paid by many lapidaries for prime turquoise from anywhere. Nonetheless, Bisbee's many mineral collectors remained less than impressed. We were put off by the price. A good piece could commend hundreds in the lapidary market. Few were the collectors who would pay the going price.

GLANCE CONGLOMERATE:

As is always the case, the characteristics of the hosting rock played a key role in the development and deposition of minerals that formed after the rock unit was deposited. The chemistry, porosity, and position of the hosting rock, all relative to the fluids that percolated through the host and formed the new minerals, were individually key to the how-where-why they formed.

The Glance conglomerate is composed of multiple lithologies, some of which were altered prior to being eroded and deposited in this surface, high-energy fanglomerate type depositional environment. The relative proportions of the various rock types changed over time as erosion cut down through the rocks upstream. In all, a variable mix of clast and the finely ground matrix from all of the included rock types were emplaced.

The Glance is post-ore in age; indeed, it even postdates the first supergene event of the late Jurassic /early Cretaceous eras. The supergene minerals, turquoise, malachite, and a few others (Stegen, 2005) were all the result of exotic solutions migrating from the nearby oxidizing porphyry units of the Sacramento Stock Complex. Only a portion of the Glance received the supergene fluids that resulted in the deposition of turquoise.

The portions of the Glance conglomerate of interest were deposited in a deeply incised canyon following the trace of the Dividend fault east from Sacramento Hill. The steep-walled canyon was eroded in the Naco limestone and was more than 200 meters deep at the point exposed to its fullest extent in the pit.

Stegen et al. (2005) briefly described the Glance conglomerate in the Lavender pit area as *“a purple-brown colored conglomerate with clasts of Pinal Schist, Paleozoic limestones, and the Sacramento Hill suite of igneous rocks and breccia. The limestone clasts are mineralized with gossan, copper oxide and carbonates, turquoise, and iron and manganese oxides plus limestones that are not altered. The matrix is composed of the finer-grained lithologies observed in the clasts. Malachite, brochantite, turquoise with iron and manganese oxides are found in the conglomerate matrix localized in channels along the base of the conglomerate.”* As a note to the above, the malachite and brochantite referenced were little more than thin rinds on pebbles or streaks in the matrix.

In addition to the foregoing, the Glance Conglomerate in the pit could be further described as an incompetent rock unit with poorly cemented areas and zones that exhibited discontinuous, post-deposition fracturing with high porosity. Nye (1968) commented on the source of the clasts as; *“The angularity and variations in size of the fragments in the*

Left: Subangular fragments of altered limestone, fresh limestone and Younger porphyry in Glance conglomerate with one speck of turquoise, Lavender pit Mine, 11 cm. Graeme collection.

conglomerate indicate rapid erosion and deposition of the material within short distances of its source."

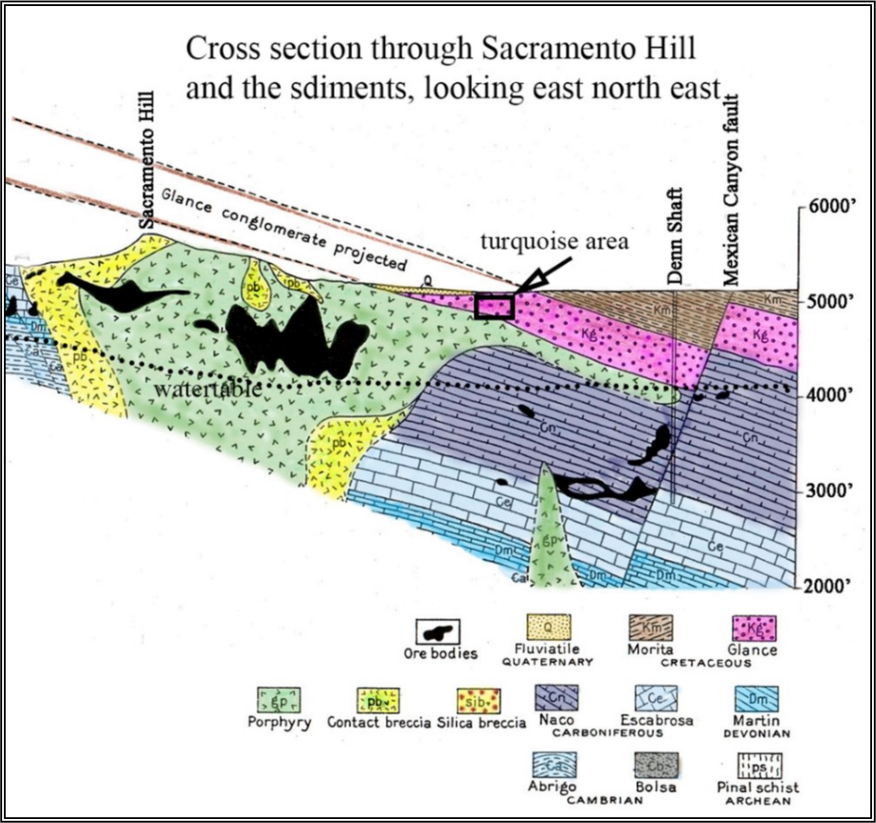
Both Cook (1994) and Stegen (2005) noted that turquoise was limited to the lower Glance. Also, it was long recognized that the lower Glance contained a large fraction of the nearby rock units, including Pinal schist and oxidized ore and altered porphyry and limestone, both fresh and altered. It was common to see angular fragments of earlier Glance Conglomerate, which had been eroded or broken by movement only to be incorporated anew in the growing conglomerate. The presence of one or more of these rock types must have been essential to the turquoise formation.

At the time of mining, the whole of the Glance was well above the existing water table. This suggests that turquoise deposition was not ongoing at this time.

The cross section to the right illustrates the relationship of those features related to the deposition of turquoise.

The post-tilting Glance conglomerate down-gradient from the chalcocite blanket in the stock complex.

Current water table, which can be interpolated to past levels.


Cross section through Sacramento Hill and the sdiments, looking east north east

With the occurrence of turquoise limited to the lower Glance and the paleo-water table derived from the chalcocite blanket just to the west, suggests that it must be post-tilting in age. This change in orientation would have given a hydraulic head pressure sufficient to cause migration of the solutions into the Glance with the necessary elements present in the solutions. Cook (1994) illustrates through the continuity of the supergene chalcocite deposition throughout the Sacramento Stock Complex that supergene activity did occur during post-inclination Laramide times and beyond.

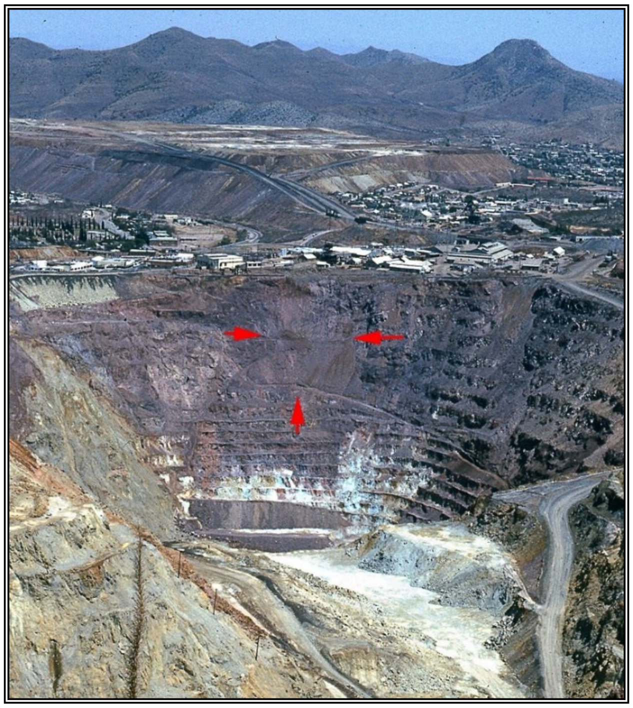
Left: The approximate location of the Glance conglomerate filled steep canyon in the Naco limestone.

The oblique view distorts the canyon walls dip. In actuality, the south wall (right) is 57^0 to 59^0. The north side is close to 70^0 and parallel to the nearby Dividend fault.

The surface trace is based on surface exposures where not covered by the Morita formation or culture.

TURQUOISE:

Turquoise from the Glance conglomerate is secondary in origin and was locally abundant. All of the turquoise found in the Lavender pit came from the post-mineralization Glance conglomerate in the northeastern corner of the pit and in the lower third part of that rock unit. Turquoise containing waste from this area was used to backfill the earlier and nearby Sacramento Pit. When removed during an expansion in 1967, it gave the mistaken impression that the Sacramento pit also produced turquoise. It did not!



Left: Glance conglomerate exposed in the Lavender Pit Mine, June, 1975. The arrows outline the area being mined at the time and the access road can be seen with a switch back gaining elevation. The highly broken nature of this rock unit is obvious.

The color of the turquoise from here ranged from nearly white to blue to sky-blue as well as to a light blue-green to, very rarely, an apple-green. Color variations within the same small piece were common. A modest amount of the sky-blue material was sub translucent in nature.

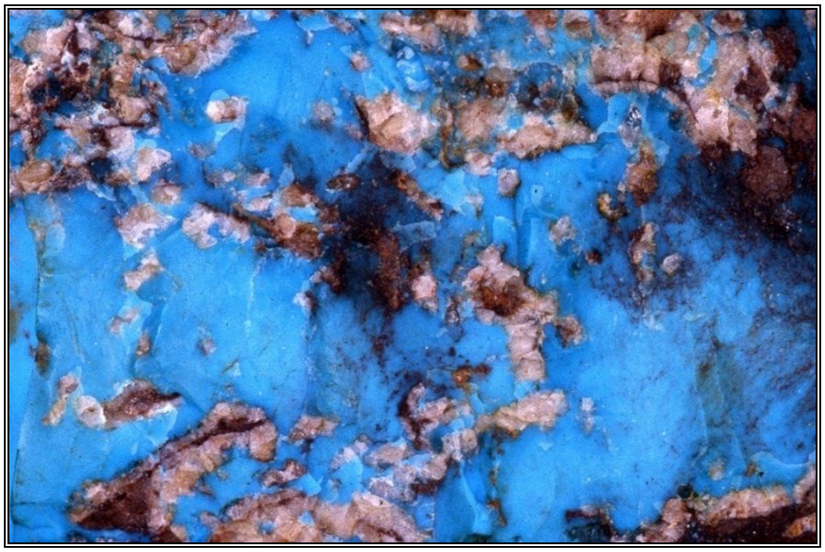
A small number of other secondary mineral species have been noted with turquoise. Chrysocolla, malachite, goethite and hematite are the more common with copper and cuprite very rarely noted. These associated species are often erosional fragments deposited with the

Glance. Ocassionally, chrysocolla was found that had been deposited as a rind on small clast in the conglomerate. For the most part, it was pale in color and friable

The turquoise occurred as open-space fillings, such as cracks in the badly fractured conglomerate. This gave the illusion of discontinuous veins.

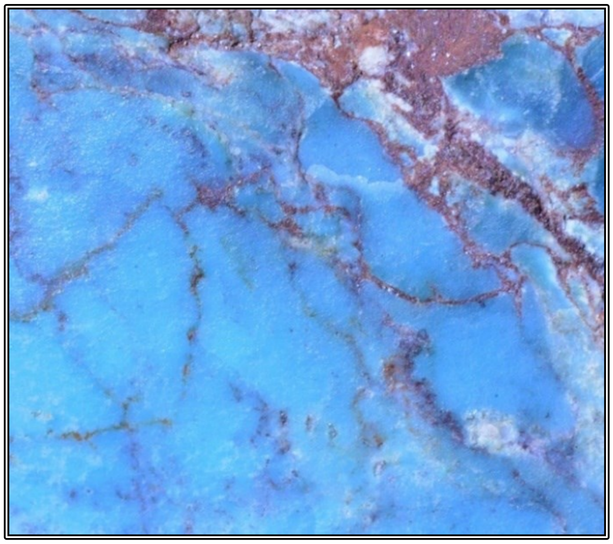
Post-Cretaceous quartz veins contained numerous crystal-lined voids, which were often turquoise filled. These made relatively handsome specimens, with the contrasting, quartz-turquoise combination. As specimens, these , were usually reasonably priced, as this material was far less desirable for lapidaries because of the substantial difference in hardness between the quartz and turquoise..

Turquoise filling of a quartz vug. Lavender pit Mine, view-7.8 cm. Graeme collection.

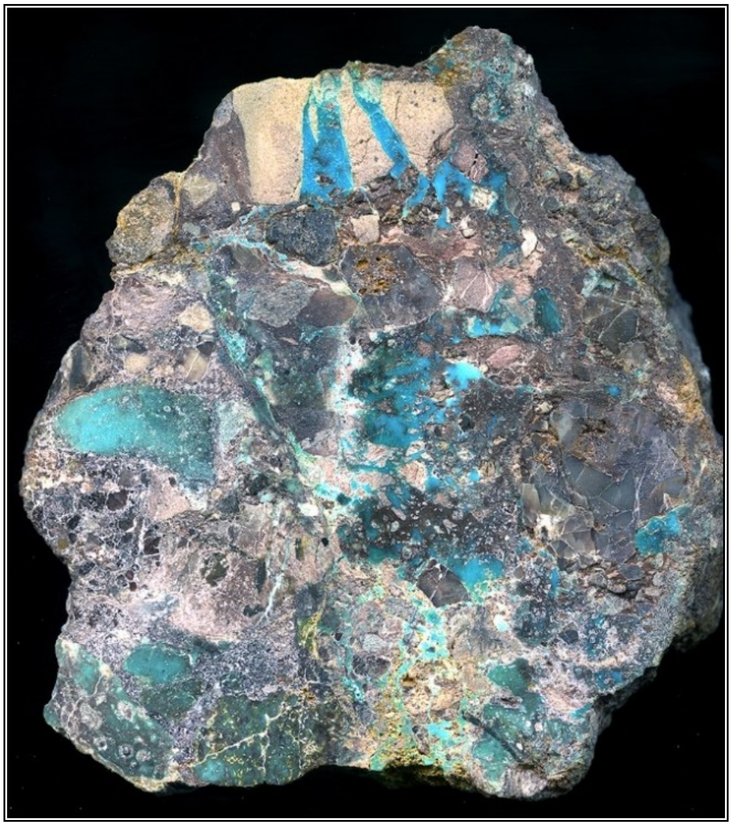


Left: Turquoise, with quartz. The differential hardness between the two species would make it difficult to polish, but ideal for a collector specimen, as the cost was typically much lower. View 2.3 cm Lavender pit Mine, Graeme collection.

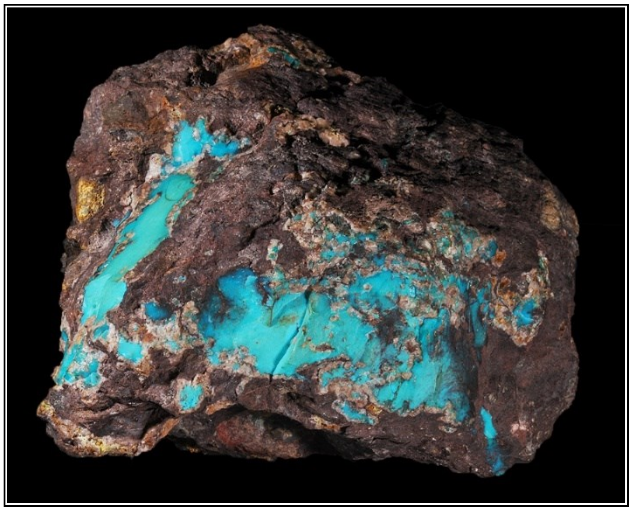
Large portions of the matrix replaced by turquoise were a common feature that was evident throughout the whole of the turquoise-bearing area. Inasmuch as the matrix was composed of small particles that were poorly cemented, the replacement would have been enhanced by particle size reacting quickly with the solutions. Less often, turquoise as a complete or total replacement of the included clast within the conglomerate was found. This seemingly random replacement was of small to mid-sized clast. Which lithologies were most favorable to replacement by turquoise is not entirely clear, but clasts of the Lowell volcanics were seen as replaced, as were some altered limestone clasts. Often, there were rinds of an unidentified white mineral between the turquoise and the unreplaced rock surrounding. The replacement of favorable portions in the matrix of the Glance, while leaving stringers of a less reactive matrix, produced the highly desirable "spiderweb" type of material.



Left: "Spiderweb" type of turquoise. View 1.3 cm. The red/brown lines are residual from the mixed lithology matrix, where the matrix contained non-favorable rock and was not replaced Note the translucence in some areas of the left-half Lavender pit Mine, Graeme collection.

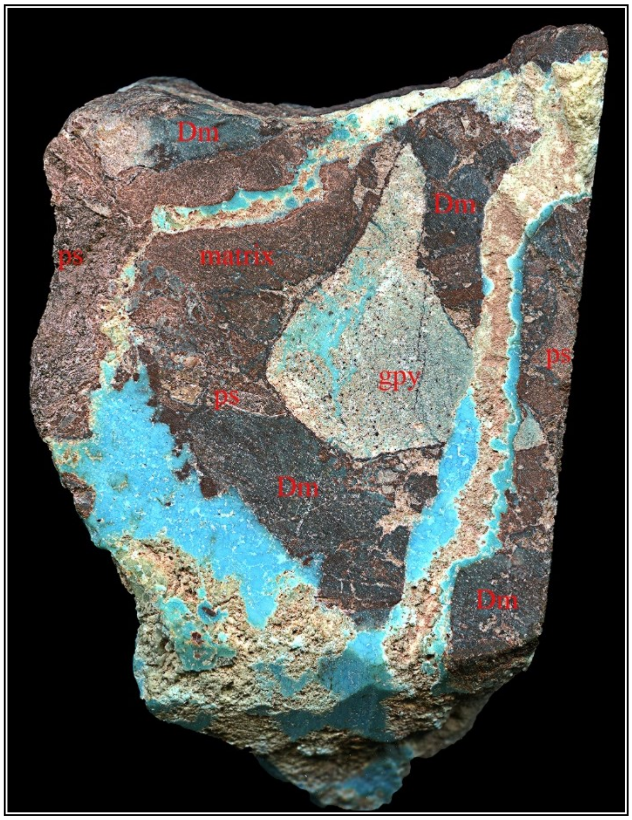


A very complex mix of lithologies composing Glance conglomerate, with turquoise as a filling of minor fractures, replacement of the matrix and as a replacement of clast of varying lithologies. Lavender pit Mine, Specimen-9 cm. Graeme collection.



Glance conglomerate, with turquoise as both a replacement of matrix and, much less so, as a replacement of tiny clasts of varying lithologies. Lavender pit Mine, Specimen-11 cm. Graeme collection.

A 3.7 cm "nugget" of turquoise, Lavender pit Mine, Graeme collection.



Glance conglomerate composed of just a few rock types – Younger porphyry (gpy), Pinal schist (ps), Devonian Martin limestone (Dm), with turquoise as both a replacement of an unidentified white vein and, much less so, as a replacement of parts of gpy. Lavender pit Mine, Specimen-11 cm. Graeme collection.

Photomicrograph of a nugget edge with white sericite (?) and an odd book of an unidentified black mica, perhaps from the Lowell volcanics. Lavender pit Mine, Vertical view-0.40 mm. Graeme collection.

POST-MINING MINERALS

Post-mining iron hydroxides and melanterite coating mine timber. Some goethite is also present from the dehydration of various iron hydroxides. The location is on the 2833 level of the Campbell mine. 1973 photo from the Graeme/Larkin collection.

Authors note: The following is mostly excerpted from our 2016 booklet, *An Overview of the Post-mining Minerals Found at Bisbee, Arizona,* which contains additional information on the subject.

As the name suggests, this is an overview of those minerals that formed after mining had opened up new, previously buried areas. When mining advanced, it brought surface to near-surface atmospheric conditions to the newly-opened areas. Oxygen, moisture, and, importantly, certain bacteria came into contact with the previously buried minerals, thereby allowing the process of oxidation to take place, beginning with pyrite (FeS_2). Pyrite was the most abundant hypogene (primary) sulfide mineral deposited at Bisbee. It is thermodynamically unstable and oxidizes, often quickly, as documented by the voluminous literature on the subject. Post-mining mineral development is based on a geochemical process identical to supergene alteration, which is discussed at length earlier in this volume.

Typical massive sulfide ore - 2433 level, Campbell Mine. Speciemen-6 cm. Graeme collection
Pyrite (brassy/yellow) is the dominate species present as abundant scattered grains and masses, along with chalcopyrite (lower right), a bornite/chalcocite/minor covellite mix (gray) and white quartz. A variety of very uncommon species consisting of largely copper/silver/gold/ sulfur coupled with tin/tungsten/antimony/vanadium/arsenic/bismuth and other elements are also present as accessory minerals in tiny, anhedral grains or inclusions in the dominant sulfides.

The process of post-mining mineral development is caused and often accelerated by the presence of oxygen and water in the newly introduced atmosphere, while the bacterium, *Thiobacillus ferrooxidans,* and other *Thiobacillus sp* are usually present and involved in a catalytic manner. If conditions are ideal, this oxidation can proceed at a very rapid pace.

Pyrite was always the dominant mineral in the hypogene sulfide deposits at Bisbee, both in the porphyries of the open pits and more so in the many scattered limestone-hosted replacement deposits mined underground. Bryant and Metz (1966) estimated that more than 500 million tons of pyrite had been deposited in the rock units hosting and surrounding the copper deposits, in the porphyries, Pinal schist, and Bolsa quartzite at Bisbee.

Pyrite occurred as huge, compact replacement masses in the limestones as well as small areas of granular material. A wide variety of other sulfide minerals were deposited, remobilized, and redeposited during the multiple phases of mineralization (Graeme, 1993). Large amounts of iron/copper/lead/zinc/sulfur-bearing minerals replaced the hosting limestones, while iron/copper/sulfur minerals were deposited in the rock units comprising the Sacramento Stock Complex.

The vast majority of pyrite found during mining was left in place underground because it was not ore but rather waste, as it contained little to no copper mineralization. This pyrite was to be both the fuel and feed for post-mining mineral development. To be sure, some pyrite was intermixed with the ore minerals and mined, but this was a relatively minor amount when compared to the total volume of pyrite present in a typical hypogene replacement deposit at Bisbee. In the Sacramento and Lavender open pit mines, the ores were very different and occurred as a very thin, supergene (secondary) coating of chalcocite and similar secondary copper sulfides on pyrite grains. Thus, unlike underground, substantial pyrite was mined with the copper sulfides. The remaining pit walls are extremely rich in pyrite and continue to produce a variable suite of these post-mining minerals.

As pyrite oxidation is an exothermal process, the exposed pyrite generated heat during oxidation, often substantial heat. Mining through the transition zone from oxide ores to sulfide ores, where oxidation was naturally occurring, was always hot, with air temperatures frequently reaching 34^0 + C (93^0 F). Underground, in areas with granular or sand-like pyrite, the large surface area presented by the many-particle faces promoted rapid oxidation, generating sufficient heat to ignite the supporting timbers or even self-combust by friction-generated heat if ground movement occurred (Mitke, 1920).

Pyrite-fed mine fires were a constant problem at Bisbee from about 1900 to the end of mining, with some fires above the water table undoubtedly still active. Water pumped into the burning areas, exited with a low pH, and highly charged with iron and copper and was captured for copper recovery. Later, interesting post-mining minerals formed where these waters ponded or seeped through surrounding rock.

There can be little doubt that many, if not most, of the species, now recognized only as post-mining, had formed during the natural, supergene alteration process before mining began. Further, many of these species were surely encountered during mining in the transitional zone between the oxides and sulfides ores.

DEPOSITION:

Post-mining mineral deposition occurs in several ways at Bisbee. Most such minerals are sulfates, which are deposited as the natural processes of sulfide oxidation began during and continued after miners made their openings for either exploration or exploitation. Minerals, other than sulfates, formed as post-mining deposits as well but were relatively minor in occurrence. In some cases, the non-sulfate, post-mining minerals were also a direct result of the sulfide oxidation, such as causing elemental copper to replace iron/steel pipe and rail. In reactive environments, such as limestone, carbonates are typically formed. Natural groundwater channels interrupted by mining caused aragonite and calcite to be deposited in the mine workings, often in substantial volume.

Fire-related minerals were few, as the underground fire areas were usually flooded with water or a slurry of mill tailings before being reopened, if ever possible. This would dissolve any of the hydrated sulfates. No fumarole-like vents existed at Bisbee, as the fires were never opened to the surface while mining, but rather the fire areas were sealed and put under positive air pressure to control fire gasses from leaking.

A list of those species recognized as forming under post-mining conditions is presented below:

alunite
alunogen
anglesite
anhydrite
anthonyite
antlerite
aragonite
aurichalcite
azurite
basaluminite
bianchite
bilinite
boothite
botryogen
brochantite
calcite
chalcanthite
chalcocite
chrysocolla
copiapite
copper
coquimbite
cuprite
cuprocopiapite
epsomite
ferricopiapite
fibroferrite
goethite
goslarite
gypsum
halloysite
halotrichite
hexahydrite
hydrobasaluminite
hydrozincite
ilsemannite
jokokuite
lime
malachite
melanterite
metavoltine
paratacamite
paracoquimbite
pickeringite
ransomite
plumbojarosite
rhomboclase
römerite
rozenite
siderite
siderotil
sulfur
szomolnokite
voltaite
zincobotryogen
zincocopiapite

Table 10: Post-mining mineral species recognized at Bisbee

More detail on the post-mining mineral occurrences at Bisbee can be found in Anthony et al. (1995), Graeme (1981, 1993), Graeme et al. (2015), Merwin and Posnjak (1937), and Mitchel (1921a).

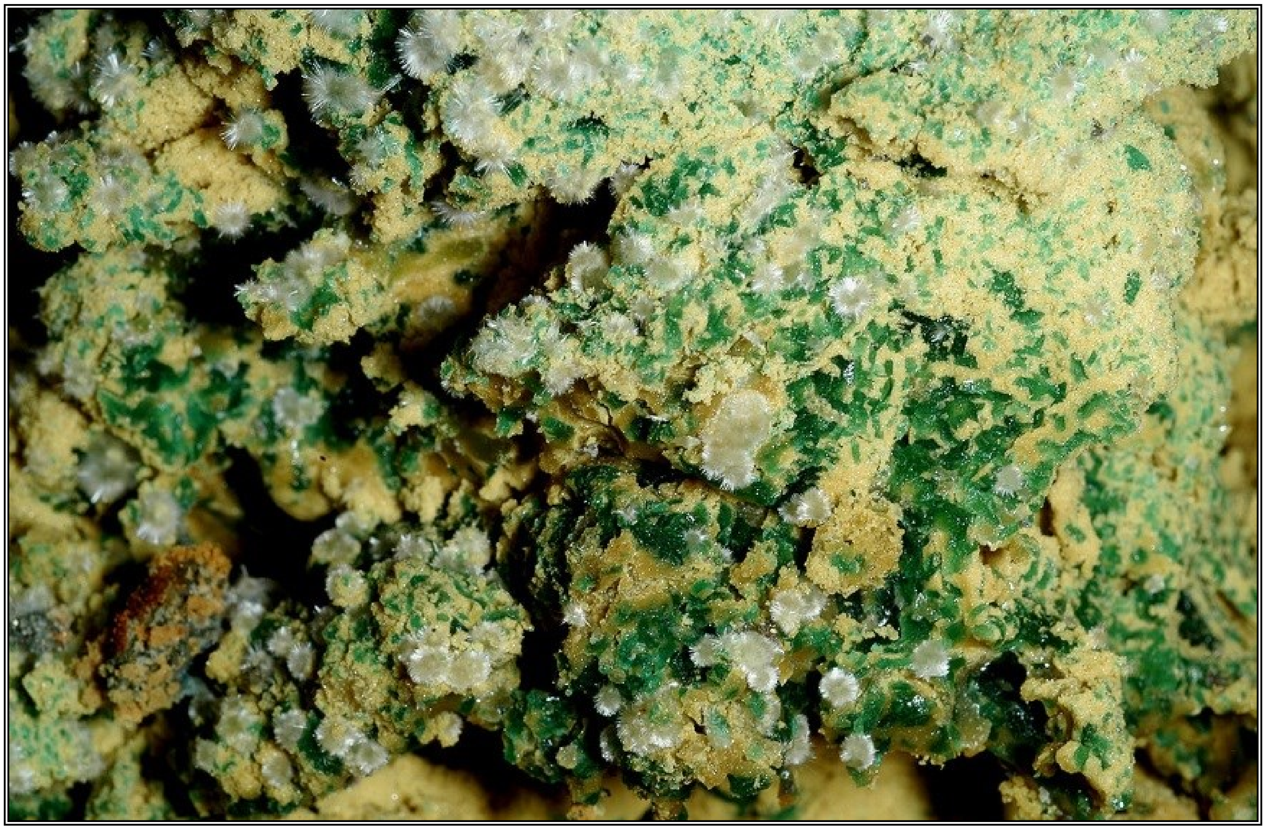
SULFATES:

The vast majority of the recognized post-mining species are water-soluble, hydrated sulfates. Post-mining sulfates were widely distributed throughout the mines and locally abundant. These sulfates develop as a result of the decomposition of the sulfides, hypogene, or supergene in the moist, now oxygenated mine environment. Pyrite is the first of the sulfides to be impacted by the newly introduced conditions. The decomposition of pyrite under damp conditions generates small amounts of low pH iron sulfate solutions that migrate along fractures and crystal boundaries to the mine openings. Iron sulfates were the most common and abundant post-mining minerals. When present, other sulfides react with these iron sulfate solutions liberating other elements, particularly copper or zinc, all be it more slowly.

Evaporation of the solutions from the mine walls and floors typically forms multi-mineral crusts with the lower pH phases at the wall surface grading to higher pH phases at the outer part of the crust, reflecting evaporation and, consequently, changing of the pH, as discussed by Merwin and Posnjak (1937). Non-reactive wall rocks such as porphyry, massive sulfides, or silicified units are essential to the development of these crust growths. While these post-mining crusts often contained multiple species, it was not uncommon for one species to be decidedly more abundant, with many of the others little more than minor accessory minerals.

In situ, massive pyrite decomposing and generating low pH solutions, which are forming iron hydroxides (brown) and have begun to mobilize copper - copper iron sulfates from other sulfide minerals. View-30 cm, 6th level Southwest Mine. Graeme/Larkin collection

In some cases, large areas of non-reactive wall rock were covered by post-mining mineral crusts. In moist, high pyrite areas, the authors have seen tens of square meters covered by post-mining sulfates, stretching dozens of meters along crosscut ribs (walls).



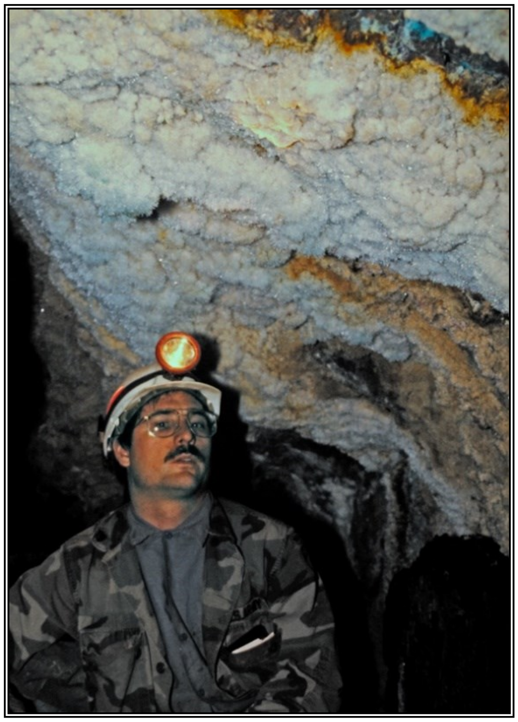
A multi-mineral post-mining, crust, in-situ, on decomposing pyrite containing at least - copiapite $Fe^{2+}Fe^{3+}(SO4)_6(OH)_2{\cdot}20H_2O$: (yellow), melanterite (cuprian) $Fe^{2+}SO_4{\cdot}7H_2O$: (Green), kornelite $Fe^{3+}(SO_4){\cdot}7H_2O$: (very light-purple spheres). In situ, 7th level, Southwest Mine, view - 16 cm. Graeme/Larkin collection

A post-mining, multi- mineral crust containing coquimbite, $Fe_2^{3+}(SO_4)_3{\cdot}9H_2O$: (purple), rhomboclase, $HFe^{3+}(SO_4)_2{\cdot}4H_2O$: (yellow-white), botryogen, $MgFe^{3+}(SO_4)_2(OH)_3$: (orange), 1600 level, Campbell Mine, view–3.2 cm. Graeme collection.

Post-mining crust of coquimbite, $Fe_2^{3+}(SO4)_3.9H2O$: (light purple), paracoquimbite, $Fe_2^{3+}(SO_4)_3{\cdot}9H_2O$:(light purple), copiapite, $Fe^{2+}Fe^{3+}(SO_4)_6(OH)_2{\cdot}20H_2O$: (yellow), melanterite $Fe^{2+}SO_4{\cdot}7H_2O$: (white), voltaite, $K_2Fe_5^{2+}Fe_4^{3+}(SO_4)_{12}{\cdot}18H_2O$: (black). Lavender Pit Mine, view – 8 cm. Graeme collection.

Single species development along mine openings was quite common. Typically, the areas that hosted a single or very few post-mining species were somewhat dryer and/or contained only modest amounts of sulfide minerals. Thus, the oxidation and the development of the post-mining mineral/minerals were both slower and more limited in extent. Other factors, such as just a single sulfide species present, could also contribute to the development of just one post-mining species or a decidedly dominant species.

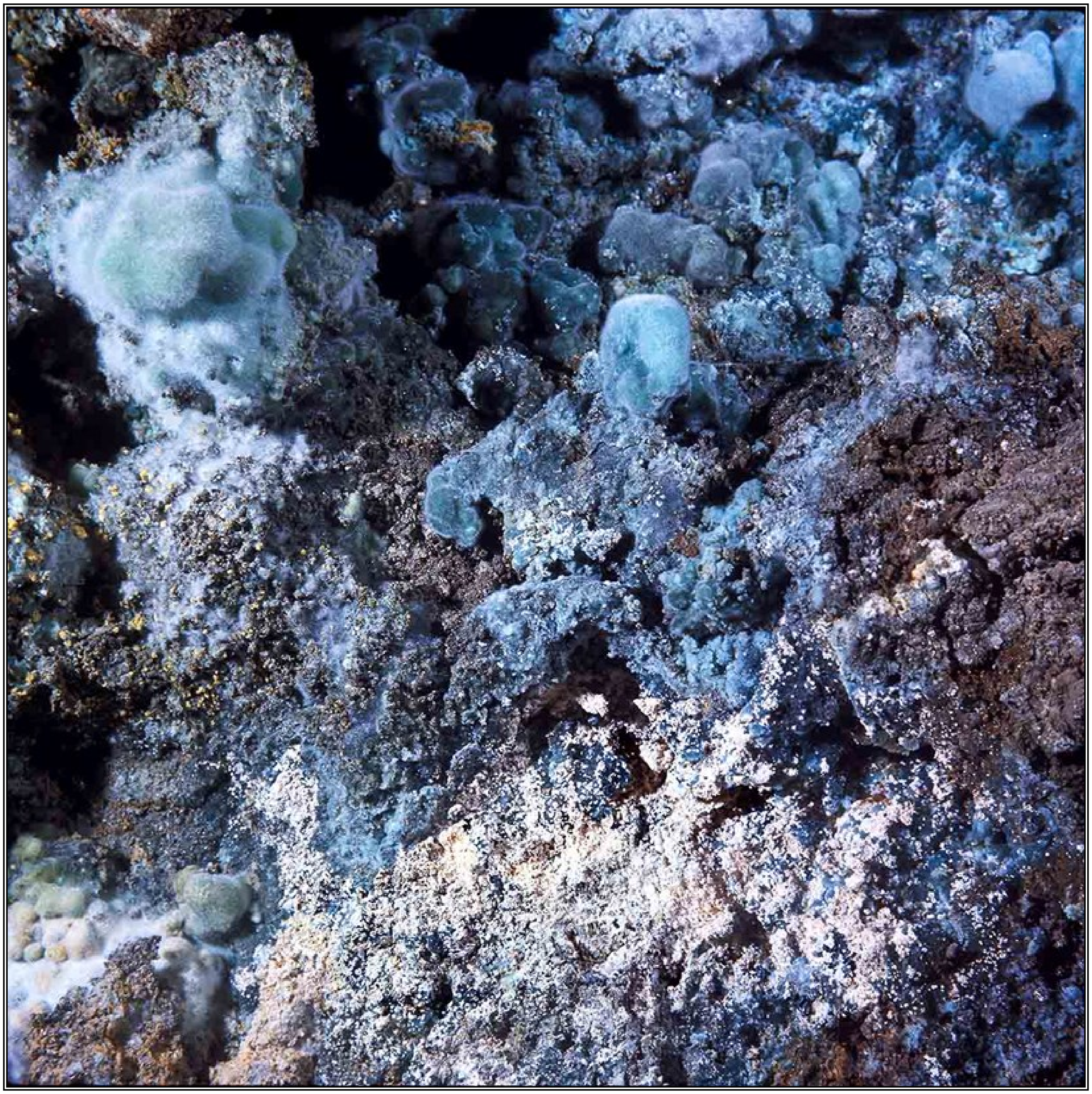
In situ, silky halotrichite, $Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$, on massive silicious pyrite, 1600 level, Campbell mine, View – 50 cm. Graeme/Larkin collection.



Melanterite, $Fe^{2+}SO_4 \cdot 7H_2O$, as a two-cm thick white crystalline crust on high-pyrite wall rock, 6th level, Southwest Mine. Author RWG IV is in the photo. Graeme/Larkin collection.

Melanterite, $Fe^{2+}SO_4 \cdot 7H_2O$, as yellow-brown crystals to 4 cm and still being deposited on broken timbers below a mined-out stope. 2833 level Campbell Mine. Author RWG III is in this 1973 photo. Graeme/Larkin collection.

White epsomite, $MgSO_4.7H_2O$, efflorescing from Martin limestone, with iron hydroxides as a paint-thick layer on the limestone, 6th level, Southwest Mine: view – 1.35 meters. Graeme/Larkin collection.

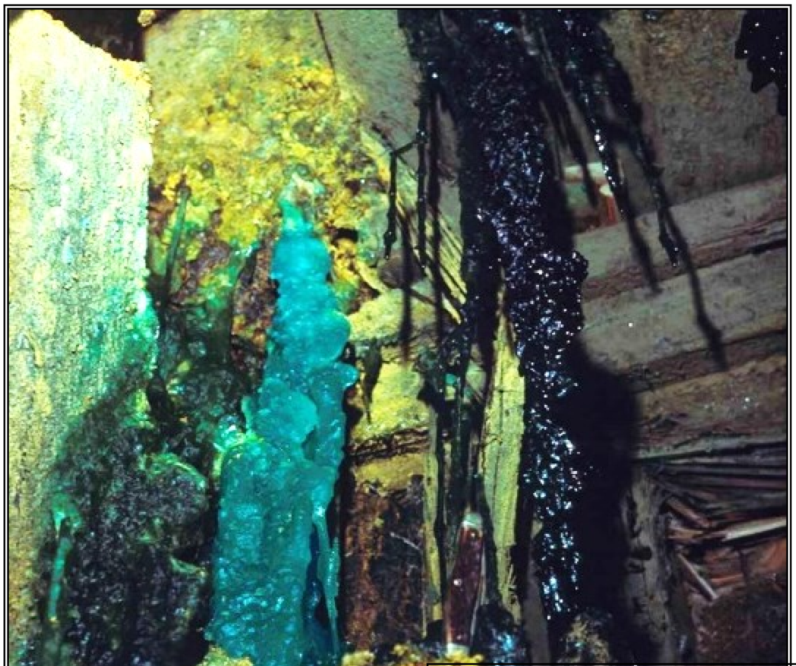


In situ, blue ransomite, $Cu^{2+}Fe_2^{3+}(SO_4)_4\cdot 6H_2O$, with minor white melanterite, $Fe^{2+}SO_4\cdot 7H_2O$, on mineralized limestone with abundant pyrite, 1800 level, Campbell mine: view-35 cm. 1973 photo, Graeme/Larkin collection.

Under conditions where more water is available, other types of growths develop with distinct crystals uncommon. Stalactites and, less commonly, stalagmites forms were common where dripping solutions were present. These forms are generally composed of a single mineral species that was dominant in the area and reflected the source mineralogy; due to a single source for the solutions and a relatively consistent pH, as opposed to multi-mineral crust in more moist areas.

As the local environment changed by mine ventilation bringing in the dryer/moister and/or warmer air or the already minor flow of water from the wall rock increasing/decreasing, the mineralogy may change. Lower or higher hydrated minerals can replace the earlier species, or new, additional species may form with or from the earlier minerals.

It was not particularly uncommon to find copper, zinc, or iron-containing varieties of the dominant species locally intermixed as distinct masses or formations with the more prevalent species. Perhaps this is due to solutions from an additional source or the exhaustion of an element at the same source. An example is the presence of pisanite (cuprian melanterite) stalactites that were noted with similar stalactitic forms of melanterite and/or chalcanthite.



Left: Chalcanthite, $Cu^{2+}SO_4 \cdot 5H_2O$: (blue), with cuprian melanterite, $Fe^{2+}SO_4 \cdot 7H_2O$: (near - black green) on copiapite, $Fe^{2+}Fe^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$: (yellow) coated mine timber. 2833 level, Campbell Mine, vertical view - 61 cm. Graeme/Larkin collection.

Right: Goslarite, $ZnSO_4 \cdot 7H_2O$: as stalactites on mine timber. 1500 level, Junction Mine. Vertical view - 1.25 meters. Graeme/Larkin collection.

Chalcanthite, $Cu^{2+}SO_4 \cdot 5H_2O$: as stalactites and stalagmites in a mined-out stope. 2300 level, Junction Mine. The formations in this photo developed in ± 20 years. It was still actively growing when the photograph was taken in 1973. Graeme/Larkin collection.

Broken sulfides scraps left underground in damp; non-reactive environments often developed sulfate coatings. These ranged from thin veneers to layers a centimeter thick. Lumps of massive pyrite were frequently completely decrepitated and replaced by a post-mining sulfate, while relatively pure massive bornite, chalcopyrite, and chalcocite had only a surficial alteration depending on the original sulfide mixture. Chalcocite-dominate sulfide ores alter to chalcanthite;

bornite alters to brochantite and/or antlerite, while chalcopyrite alters to devilline in a moist environment and chalcanthite if very wet conditions are present.

Chalcanthite, $Cu^{2+}SO_4 \cdot 5H_2O$: (blue) on chalcocite and (green) brochantite, $Cu_4^{2+}(SO_4)(OH)_6$: on bornite as alteration coatings on broken ore left behind. In situ, 6th level, Southwest Mine, view – 1.20 meters. Graeme/Larkin collection.

Galena

Left: ponded, low pH water with iron hydroxides forming as “rafts” on the surface and edges. Tunnel level, Higgins Mine, near the Wolverine Interior shaft. Graeme/Larkin collection.

Right: ponded low pH waters depositing iron sulfates due to evaporation. 2833 level, Campbell Mine. Graeme/Larkin collection. For scale; the mine workings are approximately 2.2 meters wide.

acquired a thin coat of anglesite, and the typically iron-rich sphalerite formed goslarite and a few other zinc sulfates, depending on the relative abundance of pyrite. However, even modest amounts of intermixed limestone with the broken sulfides either inhibited or prevented sulfate crust formation altogether through buffering acid formation.

Where acidic solutions formed stagnant ponds, it was common to find crystals, often large, of several of the sulfates intermixed. Chalcanthite, melanterite, as well as large, colorless epsomite crystals were the most common species in the ponds as strikingly beautiful but ephemeral specimens.


Geologist Gary Dunlop collecting cuprian melanterite and epsomite crystals from ponded mine waters on the 2700 level of the Junction mine. 1973 photo. Graeme/Larkin collection

A change in the mine environment to warmer, dryer conditions often occurred as the available water drained from the rock and sulfide decomposition continued, an exothermic process, warmed the air. Modifications in mine ventilation also altered the nature of the environment as well by changing the airflow and bringing in drier or increased volumes of air. These changes frequently caused dehydration of the original sulfates, with new species such as hexahydrite replacing epsomite and rozenite or siderotil replacing melanterite.

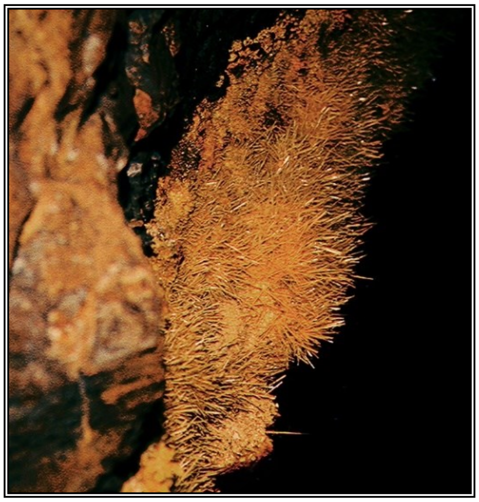

Römerite, $Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 14H_2O$: growing on pyrite-rich porphyry in the Lavender Pit Mine, View-80 cm. Graeme/Larkin collection.

The exposed sulfides in remaining porphyries and the heavily pyritized Pinal schist of the Lavender Pit Mine develop an interesting, albeit typically short-lived, suite of post-mining minerals as well. The periodic rains filter through the broken wall rock and form spotty efflorescent growths of usually iron sulfate species. However, bluish blossoms of ilsemannite can be seen on occasion, betraying the highly localized and uncommon presence of molybdenum. For the most part, these sulfate growths only last until the next rainfall, when they are dissolved, or the more typical dryness of the Arizona air returns, which causes their dehydration and decrepitation.

Very few examples of the hydrate sulfates from Bisbee have been preserved, as most quickly dehydrate on exposure to the dry, surface-atmosphere and either alter to other, less hydrated species or completely decrepitate due to the loss of water from the mineral structure. Many were the miners or mine visitors who collected brilliant blue samples of the abundant chalcanthite or cuprian melanterite, only to have it turn into an uninspiring white, chalklike mass within a few days in the dry surface-atmosphere as it lost its water of hydration and altered to another mineral, usually white or yellow/white.

This tendency for the rapid dehydration of some of the sulfates has complicated their study. When collecting these minerals, one must go prepared to preserve, as much as possible, the humid conditions before removal from the location of deposition by using airtight containers. Then, storage, once removed from the mine, must be considered. Even with the best of planning and efforts, most of these species will still dehydrate with time. Indeed, few truly remain unaltered.

Fortunately, several sulfate species do survive. Excellent examples of gypsum, römerite, voltaite, copiapite, coquimbite, paracoquimbite, botryogen, szomolnokite, and zincobotryogen are in several collections. Post-mining antlerite, brochantite, devilline, and langite are also well represented as interesting but usually uninspiring specimens.



Left: Ponded acidic waters to 25 cm. deep, in a limestone crosscut, 6th level, Southwest Mine, vertical view - 2.30 meters.

Abundant yellow/white, post-mining gypsum, variety selenite formed at the limestone- acid/water interface as thick masses of crystals, often exceeding seven centimeters in length, as shown above. View -30 cm.
Both photos Graeme/Larkin collection.

Gypsum, $CaSO_4 \cdot 2H_2O$, as selenite on post-mining copper, 2200 level, Campbell Mine, specimen - 7cm. Graeme collection.

This specimen formed in a very small pond of low pH-high copper solutions in a limestone crosscut bottom. Little to no iron was present in the solutions, something not too common.

Gypsum, as the variety selenite, was common in stagnating ponded, low to moderate pH mine waters as well, but never in association with an abundance of other sulfate species, as the necessary calcium carbonate partially neutralized the solutions. Selenite often occurred as a growth on limestone walls of flooded drifts or on the bottoms of the ponds, but always on or very near limestone. Many hundreds of post-mining gypsum specimens, variety selenite, were collected at Bisbee and are frequently seen in collections.

One other post-mining sulfate worth noting was a single occurrence of post-mining alunite, which was “actively oozing from a fracture on the 1300 level station of the Cole Mine in the 1960s. It was light blue in color and frequently “harvested” by the miners as it grew in size. However, once on the surface for a few days, it would craze upon dehydration, becoming quite fragile and much lighter in color.

IRON HYDROXIDES:

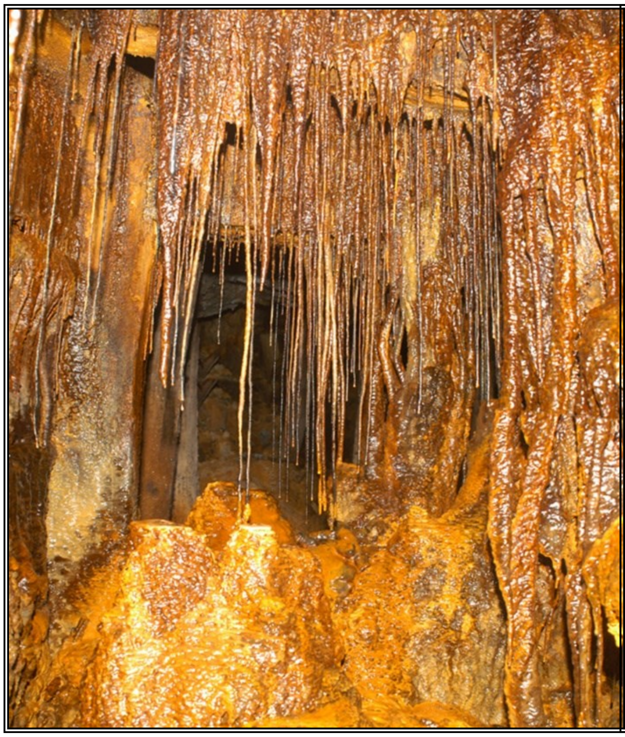
Pyrite oxidation in wet areas usually generated copious amounts of various iron hydroxides. The precipitation of the gelatinous iron hydroxides was a problem caused by these low pH solutions. If left unattended, mine workings would fill to a depth of a meter or more with troublesome slime. It is this iron-laden, low pH water that is much a part of the surface environmental problems associated with pyrite degradation, often referred to as “acid mine drainage.”

Mine waters often ponded behind rock-falls or mine timber failures in many abandoned areas. In sulfide areas, the solutions dammed-up behind these obstructions often filled with thick yellow mud, consisting of iron hydroxides, which had precipitated out of the high-iron solutions. Sometimes the mud would be waist-deep. Walking through such deep unconsolidated mud often released mini-locallized floods held by dams of mud . If undisturbed, goethite rafts formed on the surface in still areas and eventually sank to the pond bottoms.

Goethite raft accumulation with calcite. 6th level, Southwest Mine. This is not post-mining, but formed in the same manner and demonstrates the results of sinking rafts. View- 25 cm. Graeme/Larkin. collection.

Ponded acidic mine water depositing iron hydroxide muds in abandoned working, note abundant white to brown melanterite on ceiling and walls, 6th level, Southwest Mine, horizontal view – 2.8 meters. Graeme/Larkin collection.

Acidic mine water formed by the oxidation of pyrite. Mud-like iron hydroxides have precipitated from the water and partially filled the mine opening. Tan colored melanterite locally coats the mine walls. 7th level, Southwest Mine, horizontal view – 2.2 meters. Graeme/Larkin collection.



Iron hydroxide stalactites and stalagmites deposited by the acidic water that have partially filled the mine opening. 7th level, Southwest Mine, vertical view–2.3 meters. Graeme/Larkin collection.

Acidic mine water with stalagmite-like forms and minor melanterite. 6th level, Southwest Mine, view – 38 cm. Graeme/Larkin collection.

While some of these hydroxides were deposited as little more than a slimy mud in the workings, others often formed numerous long stalactites and massive stalagmites. Undoubtedly, some of the same iron compounds were deposited in both cases, but no effort was ever made on the part of the authors to determine either the chemistry or mineralogy of any, but rather to simply document the appearance during deposition and, in some instances, note the ultimate apparent end minerals, which formed with dehydration.

In areas with substantial dripping water, which had passed through the oxidizing sulfides, impressive clusters of yellow to yellow/brown to dark brown stalactites would form. In several instances, the stalactite/stalagmite development was such that it nearly closed the mine opening.

For the most part, the stalactitic growths were delicate, not soft, but rather hollow and/or composed of successive layers of material that were poorly cemented together. Often stratus of solution were in between the concentric, crust-like layers.

Right: Goethite coating "limonite" stalactites that formed in a similar manner to those above. Specimen – 11 cm. Shattuck Mine. This piece is not of post-mining, but shows the open spaces between layers. Graeme collection.

On drying over an extended period of time, the iron hydroxides became an impure mixture of several iron oxides but were predominantly goethite and lepidocrocite. In any event, the collective term "limonite" best describes the appearance of the ultimate product.

CARBONATES:

Aragonite:

The most common of the post-mining carbonates was aragonite. During the course of mining through the barren limestone host rock, it was common to intercept cracks, faults, and solution channels that served as conduits for the usually small amounts of water within the limestone. Most often, the water in these openings was clean and metal-free but high in dissolved calcium and CO_2. As the water entered the mine openings, it began to liberate the CO_2 and deposit calcium carbonate, usually as aragonite, though calcite was deposited in some areas. The reason for the apparent significant preferential formation of aragonite over calcite is unclear but may well be related to the relatively high kinetic energy associated with the deposition – cascading or fast flowing or long vertical drop of the depositing waters.

A one-gallon bucket coated by post-mining aragonite. 6th level, Southwest Mine. Graeme/Larkin collection.

In limestone areas, post-mining aragonite was a common occurrence in most of the mines. Aragonite stalactites of several centimeters in length, often coated with small, acicular aragonite crystals, were locally abundant where the groundwater flow was modest. In mine openings that served as main ventilation ways, these stalactite-like formations would grow directed into the strong airflow almost parallel to the mine back (ceiling), but without the acicular crystal growth on their exterior. With moderate groundwater available, the walls and back could be covered with parallel aragonite growth reaching ten centimeters, and all pointed into the wind, where evaporation took place the most rapidly.

The apparent rapid rate of deposition of aragonite was noted in several places, but perhaps the most interesting, in our view, is a single, one-gallon, galvanized steel bucket left by lessees in early 1944 on the 6th level of the Southwest Mine. It had been placed under a steady drip of clean water to use for drinking, as suggested by the remains of a wooden water keg close by. It would have taken several hours for the bucket to fill, yet when first found some 30 years later, a full three centimeters of semi-pearlescent aragonite had been deposited where the water flowed from the vessel. Today, more than five centimeters of aragonite have encrusted the lip of one side, and the whole of the bucket is coated, representing some two centimeters of additional deposition in less than 45 years.

Thick, massive post-mining aragonite was abundant in several places where large volumes of mine water were transferred from level to level down 100-foot raises. Ladders and other timber were often coated with 5-10 cm of aragonite by the forceful, cascading waters. The most memorable is a raise between the 300 and 400 levels of the Czar Mine that channels water from under Queen Hill. These clean waters were kept separate from other mine water and collected for use on the surface in boilers, showers, etc., during the operation of the mine.

Two views of an 8 cm. aragonite stalactite-like form that grew over broken mine timber in about 25 years. The color variation in the top view, reflects changing water quality from turbid to clear. 2300 level, Junction Mine. Graeme collection.

Near pure-white aragonite to 10 centimeters thick, coated all of the timbers, in spite of the force of the hundreds of liters per minute cascading down the 100-foot raise. The receiving crosscut was flooded, as the 400-level station had collapsed sometime in the early 1950s, so the timber below the water level was somewhat less heavily coated by aragonite. As the rock damming up this significant flow was very course, the water passed through it quickly, precluding the formation of aragonite/calcite rafts, so commonly seen covering still mine waters. Fortunately, good, natural ventilation kept the concentrations of liberated carbon dioxide low, allowing entry, as the water nearly filled the crosscut, forcing one to swim in the frigid water.

A second very similar site was on the 2300 level of the Junction Mine, where the waters from the Denn Mine poured down a timbered raise from the level above on their way to the 2700 level pump station. For the most part, this water came from the wide Dividend Fault zone, cut when sinking the Denn Shaft in the 1930s. Over time, the water quality appears to have changed, no surprise as substantial mining was taking place. The change in water quality is reflected in the variable coloration of the deposited aragonite. As mining passed well below the 2000 level, the flow decreased, and some coloration due to copper was imparted. By the early 1970s, just a few tens-of- liters per minute were flowing down this raise, a fraction of what company records noted some 30–40 years before.

Post-mining aragonite "cave pearls" to 2 cm, 2300 level, Junction Mine. Graeme collection.

The diminished flow allowed for the formation of colorful blue/green rafts along the still margins of the ponded water. Similarly, colored cave pearls to two centimeters in size formed where a small flow of water fell from a displaced mine timber into a small, otherwise still pool.

Post-mining aragonite from the floor of 12 XC, 2700 level, Campbell Mine, as can be seen in the below photo. Specimen – 7 cm. Graeme collection.

As exploration east of the Campbell Mine progressed in the early 1940s, substantial amounts of water were hit, as expected. While every reasonable precaution had been taken, the Campbell Mine was partially flooded in 1941 by a flow from 12 crosscut (XC) on the 2700 level, estimated at more than 200,000 liters per minute (Mills, 1958).

Right: Water door on 12 XC, 2700 level, Campbell Mine in 1962. Vertical dimension – 2.8 meters. Note the abundant post-mining botryoidal aragonite between the mine rails. Graeme/Larkin

After months of pumping, access was regained, but substantial water still flowed from a series of subparallel faults in the mine wall. By 1960, thick, travertine-like aragonite, as much as three centimeters thick-coated the crosscut floor, and the water was still flowing 25 centimeters deep across the whole of the two-meter-wide crosscut floor. A match lit a meter above the flowing water would quickly be extinguished if lowered a bit by the high CO_2 concentrations due to the rapid degassing of the groundwater. This degassing, of course, caused the relatively rapid precipitation of aragonite. The miners locally called this aragonite “brooksite.”

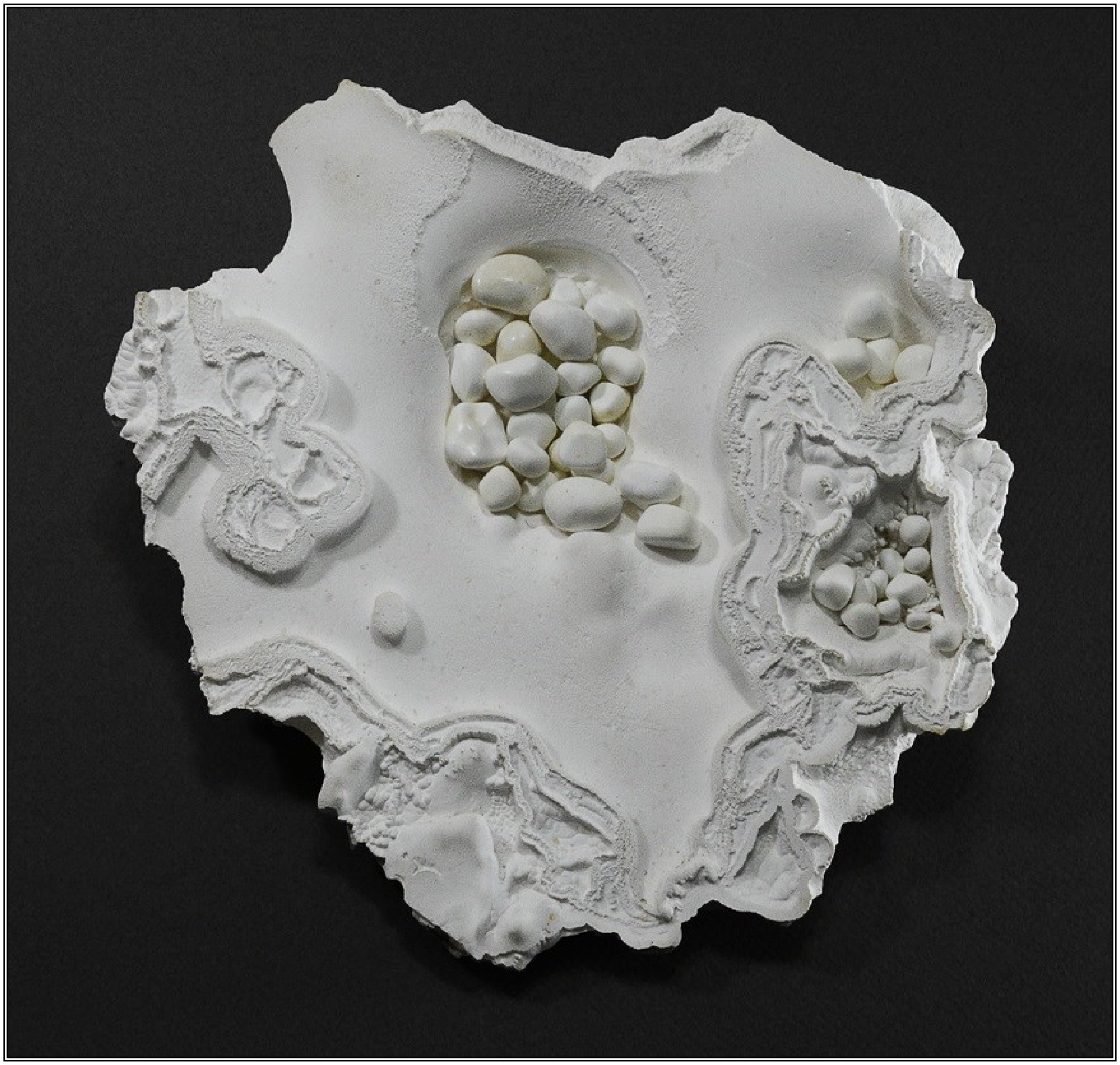
Specimens of the tan to yellowish to gray, flowstone-like aragonite collected from the fast-flowing water often contain angular fragments of fresh limestone or sulfides as well as anything else thrown aside, such as wood, nails and broken light bulb pieces, even pieces of forgotten native copper, which were placed in the water for cleaning; a common way to clean copper.

On the 2200 level of the Campbell Mine, an unusual blue-colored post-mining aragonite/calcite mixture formed in small amounts on and under a leaky wooden flume. The flume was constructed to capture water pouring from a two-inch diamond drill hole and carry it over a gobbed stope to a water ditch. This aragonite clearly shows ripple-like features and is occasionally stalactitic when it formed on the bottom of the flume. The reason for its striking blue color is unknown, but it is reasonable to assume a high degree of copper substituting for calcium in the crystal lattice. More than a few have thought this material was azurite, as can be seen below.

Aragonite/calcite – Front and back views of a 13 cm. post-mining aragonite and calcite mixture. This formed on a leaky, timber flume used to conduct water over broken ground. The pattern of the wood is clearly visible on the back side. 2200 level, Campbell Mine. Graeme collection. The intense blue color of this material caused it to be confused with azurite, but it is largely aragonite more or less altered to calcite.

Right: Aragonite "Bird's nest," with splinters of mine timber, 2200 level, Campbell Mine, specimen - 9 cm. Graeme collection.

From a mineral collector's point of view, the post-mining aragonite forms, which the miners call "bird's nest," are a much-coveted prize. These interesting forms developed in inactive limestone areas of all mines, in still-air environments, and from slow dripping solutions. These were flat deposits, cementing small areas of the loose rock of the mine floor, with a depression developed where the constant water drops hit. Small rock fragments within the depression would be coated with successive layers of aragonite, resulting in rounded growths, much like cave pearls that resembled small eggs. Thus, the local name.



An uncommonly fine aragonite "Bird's nest," 2200 level, Campbell Mine, specimen - 27 cm. Graeme collection.

These interesting forms were usually white, but bluish copper-tinted, and red to brown iron-colored examples were not uncommon. While "bird's nests" were not truly rare in the mines, successfully collecting one was a real challenge. Thus, a few good examples exist.   It took some years, often decades, for the slow deposition of aragonite from a single dripping source to become thick enough to withstand the force needed to remove one, even though they formed on the broken rock or compacted fill on the mine floor.

Aragonite "Bird's nest," forming adjacent to a pool of water. 6th level, Southwest Mine, view - 25 cm. Graeme/Larkin

Miners were known to find a developing "bird's nest" and hide it by placing old mine timber to protect it from view and/or prevent someone from stepping on the delicate treasure. They also often began the task of preparing for removal by driving large nails around the area to develop cracks and would use strips of canvas to control the splash area into the area of interest. More than one miner would add a small bit of chalcanthite on occasion to enhance the color. However, no matter the care and planning taken, it was usually luck that allowed for a successful recovery. Over our many years of viewing Bisbee minerals, we have seen fewer than ten such specimens that are of any real aesthetic interest.

Calcite:

Post-mining calcite was also widely distributed and common in the majority of the mines, typically forming small stalactites and thin flowstone-like ribbons on mine walls. Oddly, few crystals of post-mining calcite, other than microscopic size, are known from Bisbee. Very few post-mining calcite specimens from here were of interest to collectors.

Right: Typical post-mining calcite as small stalactites and flowstone on slightly altered Martin limestone, 6th level, Southwest Mine, view – 1.4 meters. Graeme/Larkin collection.

Post-mining calcite deposited by steadily seeping water along a wide fault zone. 2200 level, Junction Mine. Graeme/Larkin collection.

Right: A close-up view of the post-mining calcite in the above on the 2200 level, Junction Mine. View–30cm.

Note the oriented growth direction. It was into the strong airflow caused by the mine ventilation, as a huge fan was less than 100 meters distant at the Junction Shaft. Graeme/Larkin collection.

Most stalactites above aragonite "bird's nest" formations were calcite. Calcite was also formed as thin "raft" forms on top of ponded clean water. Calcite was noted coating a long-abandoned mine car under a small but steady flow of water on the Tunnel level of the Higgins Mine, a most unusual occurrence. Below are two photographs of this mine car taken a bit more than 40 years apart.

Left top: Post-mining calcite growth on a mine car, Higgins Mine, Tunnel level in 1967. More than 1/2 inch of calcite had been deposited in the just over 20 years since this mine closed.

Left bottom: The same mine car some 40 + years after the first photo; illustrating the relatively rapid calcite deposition.

The calcium carbonate rich water is flowing from a small diameter diamond drill prospecting hole.

Below: Colorless to white, post-mining calcite on copper-tinted post-mining aragonite, 6th level, Southwest Mine. Specimen – 9 cm. Graeme collection.

Malachite:

Malachite as a replacement rind on recrystallized Escabrosa Limestone, from the Holbrook Mine, specimen - 13 cm. Graeme collection

Low pH, copper laden mine waters were a significant problem at Bisbee as early as 1890 when the mining of deeper ores exposed areas undergoing sulfide oxidation. Some of the water contained several tens of pounds of dissolved copper per thousand gallons of water. Any iron, steel tool or mine rail that was in this water, for even a short time, was attacked with the iron going into solution and a useless copper form left in its place. Control of acidic mine waters, locally referred to as "copper water," was a critically crucial operating issue, even to the end of mining in 1975.

Left: Malachite as an impure replacement rind on Martin Limestone from the Czar Mine Specimen–7 cm. Graeme collection.

Note the relic features of the limestone are preserved in the replacing malachite.

During mining early on, it was a common practice to channel the acidic, metal-rich solutions through old, abandoned workings, including gobbed (backfilled) stopes, to eventually bring them to a pump station for removal to the surface for copper recovery via iron precipitation.

The gob in the early stopes was typically a mix of mine waste rock, much of it hand-cobbed limestone, sorted during mining. As early mining took place close to the Sacramento Stock Complex, hydrothermally altered limestone and porphyry waste were common in the gob as well.

It did not take long for the acidic waters to attack the limestone chunks in the gob, leaving a replacement veneer of what was usually malachite, to several centimeters thick. In some cases, the typical process for forming malachite occurred with the development and transport of copper carbonate solutions, typically gel-like, to open spaces for deposition. Such material is usually indistinguishable from most banded malachite. In gob exposed during the mining of the Lavender Pit mine, one of the authors found a piece of thick, banded malachite in the Holbrook Extension with a rusted track spike embedded within, reflecting its post-mining origin.

Sufficient copper was deposited in a number of cases to make the gob ore grade (Bateman et al. 1914). Douglas (1909) did not recognize the process and suggested that what was now ore had been placed as waste fill in the past. This also caused an erroneous belief among miners that "the old-timers used malachite as a backfill," a local myth that persist to this day.

In other environments, malachite often developed as a thin, often scaly, crust on limestone or calcite when copper-rich solutions flowed over them or in the residual broken rock adjacent to oxidizing sulfides in mined-out stopes. On rare occasions, stalactites of malachite formed on the edge of a broken rock face. In one instance, malachite was apparently being co-deposited with chrysocolla, as modest amounts of copper-laden water were comingled, with one part coming from a silica breccia and the other from fresh limestone. However, in general, post-mining malachite from Bisbee was seldom collected, as it was typically less than inspiring.

Several other copper minerals were deposited as well by the "copper water" passing through the gobbed stopes, with copper and cuprite fairly common in non-reactive backfill. Bateman et al. (1914) noted that the acidic solutions altered the less reactive rock in the fill to several of the clay minerals such as kaolinite and halloysite.

Azurite:

Post-mining azurite at Bisbee was rare. No doubt, this was a function of the higher CO_2 required for deposition than is typically found in typical mine atmospheres. Nonetheless, in a few instances, it has been recognized as a surficial replacement or along fractures in limestone along with more abundant malachite. Subaerial deposits of azurite seem to mimic malachite in that they are quite gel-like when deposited.

One extraordinary occurrence on the 3rd level of the Southwest Mine is notable. Solutions emerging from a fracture deposited botryoidal azurite over an area of more than a meter. While it was but a thin crust of three to four millimeters thickness, it was strikingly beautiful.

Other carbonate species that have been noted to form with azurite under post-mining conditions include aurichalcite. Post-mining aurichalcite was observed forming over the period of just a few days along with azurite and malachite. The aurichalcite was formed from a thin jellylike mass running into an open space and drying in a 30-cm wide goethite seam bounded by limestone (Tenney, 1913).

One of the authors (DLG) on the 3rd level, Southwest Mine where post-mining azurite is being deposited as a gel-like flow from fractured limestone below a stope. Graeme/Larkin collection.

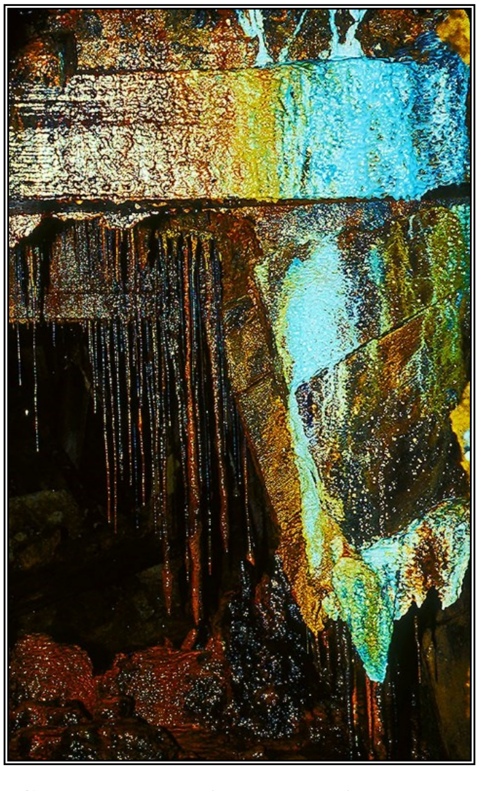
Hydrozincite in situ, on the "B" level, Copper Queen Mine where shortwave ultraviolet lighting causes the massive sphalerite to fluoresce orange-red, calcite gives a red color while the post-mining hydrozincite responds to UV light with a blue-white fluorescence, and can be seen at left-center and a bit more to the right. Horizontal view-1.3 meters

HYDROZINCITE:

Hydrozincite has been noted as a localized post-mining flow from the alteration of massive sphalerite in the Copper Queen Mine. It was also reasonably abundant as an alteration product of the massive sphalerite used as waste backfill in a small stope on the "B" level of the Copper Queen Mine. At the time the Copper Queen Mine was operating (1880-1888), the limited zinc mineralization found was not of any economic importance and thus was left in place as waste.

CHRYSOCOLLA:

Malachite, azurite, and aurichalcite formed from gelatinous materials that typically oozed slowly and in small amounts from cracks and other small openings. Chrysocolla, $(Cu^{2+},Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$, formed in a similar manner. Indeed, post-mining chrysocolla was quite common, having been found in several mines as light blue stalactitic growths and as bright blue-green flows on opening walls. Without exception, this material crazes and becomes much paler in color and friable due to desiccation when collected and taken to the surface.



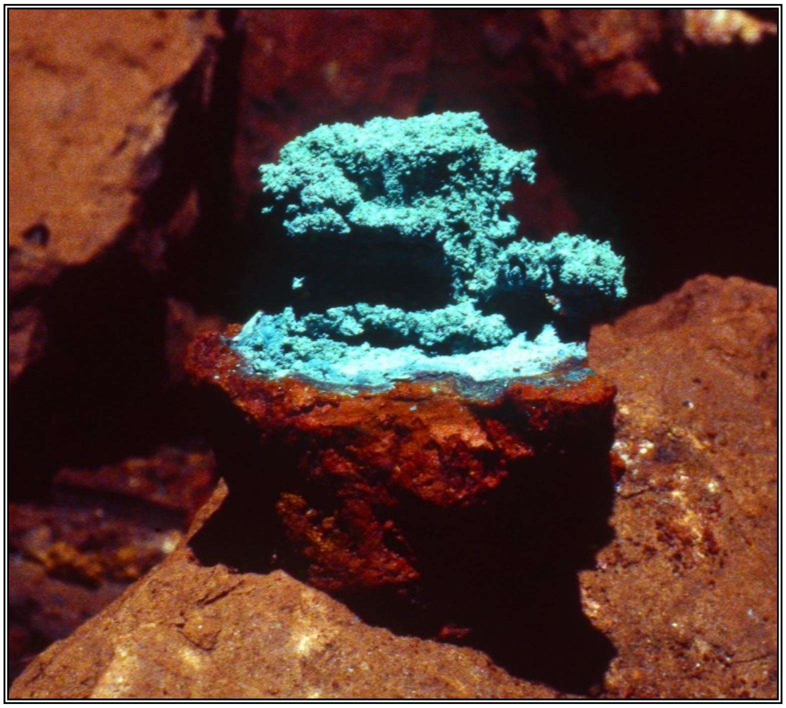
Chrysocolla and iron hydroxides, forming on mine timbers. The timber to the right is a chute for removing broken ore from the stope above

7th Level, Southwest Mine, view-1,6 meters vertical. Graeme/Larkin collection.

Chrysocolla and malachite being deposited simultaneously, in situ. Silica-rich solutions are coming from a silica breccia on the left, while carbonate-rich solutions are flowing from limestone on the right. side. 6th Level, Southwest Mine, longest stalactite – 9 cm. Graeme/Larkin collection.

CHLORIDES:

The exposure of unstable, non-sulfide minerals to the atmosphere during mining also resulted in the formation of post-mining species, often quickly. Nantokite, CuCl, and tolbachite, $Cu^{2+}Cl_2$, both copper chlorides, would react with the humid mine air to form paratacamite, $Cu_2^{2+}(OH)_3Cl$, in a matter of a few hours. In one case, a seven-centimeter cuprite nodule with a nantokite core developed a soft "ram's horn" form of scaly paratacamite three centimeters high in less than 20 hours.



Paratacamite as an 8 cm, mushy extrusion from a cuprite nodule which was filled with nantokite, and formed in less than 20 hours upon exposure to the humid mine atmosphere by breaking the nodule. In situ photo. 14 stope, 5th level, Southwest Mine. Graeme/Larkin collection

COPPER:

As noted above, low pH, copper-laden waters were common in the mines at Bisbee. These waters were solutions resulting from the oxidation of the variable and complex sulfide minerals and contained a variety of dissolved metals but mostly iron and copper. The pH of these waters was quite variable, depending on the source and, of course, dilution, but pH ranges from below two and less than four were common. If not controlled, "copper water" (a local term that will be collectively applied herein) was terrible stuff, yet it was both a bane and a blessing.

From a safety standpoint, there was nothing more uncomfortable than copper water in the eyes. From personal experience, we can say it was as painful as most any minor injury and temporarily debilitating. Skin burns from strong copper water or prolonged contact with it were unfortunately all too common and took time to heal. These were much like burns from sulfuric acid.

Operationally, everything this water contacted was damaged, iron and steel most of all. Thus, care was always taken with controlling the flow of copper water to keep it away from the mine rail and pipe. The water was then channeled or pumped to recovery plants to extract the copper via iron replacement precipitation. Many millions of pounds of copper were produced at Bisbee in this manner.

A, post-mining copper replacement of a 20.6 cm iron hammer, found in 1925 on the 800 level of the Shattuck Mine, Shattuck collection, BMHM specimen. Photo by Jeff Scovil. Used with permission.

However, once mining in an area was completed, the control of such water was no longer a priority, and small areas would pond, often covering the now-abandoned rail and all else left behind.
Copper quickly began to replace the iron and steel. Initially, the original form of the replaced item is often apparent. However, copper growth

Front and back views of mine rail replaced by copper with the copper expanding well beyond the replaced steel, 2200 level, Campbell Mine, specimen – 10 cm. Graeme collection. The yellow-brown is rust-like material from the iron.

would continue as direct precipitation of small crystals from concentrated solutions, now expanding the size of the copper mass and eventually obliteration the original form.

Mass of copper thus formed could easily exceed by ten times the volume of the original iron. Oft times, miners would collect these copper masses and sell them as "native copper." In general, these pieces were relatively bright in appearance, reflecting their time in an acid environment. The expansive Junction and Campbell mines were the sources of most of these coppers, but all of the sulfide containing mines produced similar material.

Copper that formed as a direct precipitation from solutions and not replacing steel or iron, 2200 level, Campbell Mine, specimen - 14 cm. Graeme collection.

In a few cases, copper would precipitate directly from concentrated solutions without forming around a replaced iron or steel core. Examples are shown above. These pieces tended to be composed of aggregates of tiny crystals that were more open, even spongelike or in radiating forms, and could easily be confused with naturally occurring copper. This potential confusion was often compounded by one to two-millimeter cuprite crystals that commonly accompanied these interesting pieces.

Colorless gypsum, variety selenite was also commonly found associated with the copper that precipitated from solution, reflecting an equilibrium with copper and saturation of calcium with a more moderate pH.

Gypsum, variety selenite, on post-mining copper that precipitated directly from high copper solutions. 2200 level, Junction Mine, specimen – 9 cm. Graeme collection.

Post-mining copper deposited on mine timber. Lavender Pit Mine; longest piece – 11 cm. Graeme collection.

Copper directly precipitated on mine timber has been noted in several copper mines worldwide. At Bisbee, it was found in the Lavender Pit Mine as it encroached upon the old underground working of the Sacramento Mine. To preclude the unpleasant task of pumping these acidic waters from the pit, mine planning efforts always kept a low point in the pit over abandoned underground workings, which served as a drain for the pit. All of this water was collected on the 1600 level of the Sacramento Mine and directed to an acid-water pump station on the

1800 level Junction Mine for pumping to the surface and to a copper/iron precipitation recovery plant (the 1600 Sacramento was at much the same elevation as the 1800 level Junction).

Over time, copper to five millimeters thick was deposited in voids of the usually badly broken and splintered timber. Much of this material was collected by the mineworkers as the pit advanced.

FIRE DEVELOPED MINERALS:

Mine fires were a constant problem in the district once the primary sulfides were exploited to any degree (Mitke, 1920). Pyrite would generate substantial amounts of heat during decomposition to the point of occasionally spontaneously combusting and igniting the supporting timber. The burning sulfides were a real problem because, with adequate oxygen, they could burn for a very long time – think forever, emitting toxic gases while denying access to ore in the fire area. Many of these fires defied all efforts to extinguish them and burned for years. Mine fires in both the Briggs and Campbell were contained but still burning at the time the mines were closed.

Minerals produced as a result of mine fires at Bisbee have not been thoroughly studied. The few species recognized have been noted more by chance than by design. This is because of the lack of access to the areas under conditions that allowed study. Unlike Jerome, Arizona, the fires in the mines at Bisbee were never exposed to the surface by mining. While a number of fire areas were later mined underground, they had been flooded up to the time of reentry or had been filled with a slurry of mill tailings to allow access (Sherman, 1918b; Mills, 1958). This destroyed the soluble minerals that might have formed. However, anthonyite from the Dallas Mine may well have been formed as a result of the sulfides that burned in a nearby stope during a mine fire (Anthony et al. 1995).

The 1948 fire in the Campbell mine, which started on the 2200 level, spread quickly and soon reached the 1300 level. It was eventually vented to the surface through the Oakland shaft, which had been developed for that reason (Mills, 1958) and much of the fire areas reclaimed. Portions of the 1300 level were still very hot, if not burning, in the mid-1970s. The workings closest to the fire, through which the hot gases passed, had their limestone walls somewhat calcined, producing a very impure lime (<30% available CaO on an analysis). Post-mining gypsum in a nearby area was converted to anhydrite, and in another area, tiny sulfur crystals were deposited on the mine walls. No other fire-related minerals were noted during the single visit by one of the authors to the accessible portions of the exhaust workings in 1975. Dangerously high levels of carbon monoxide gas and temperatures in excess of 55° C prevented a complete inspection.

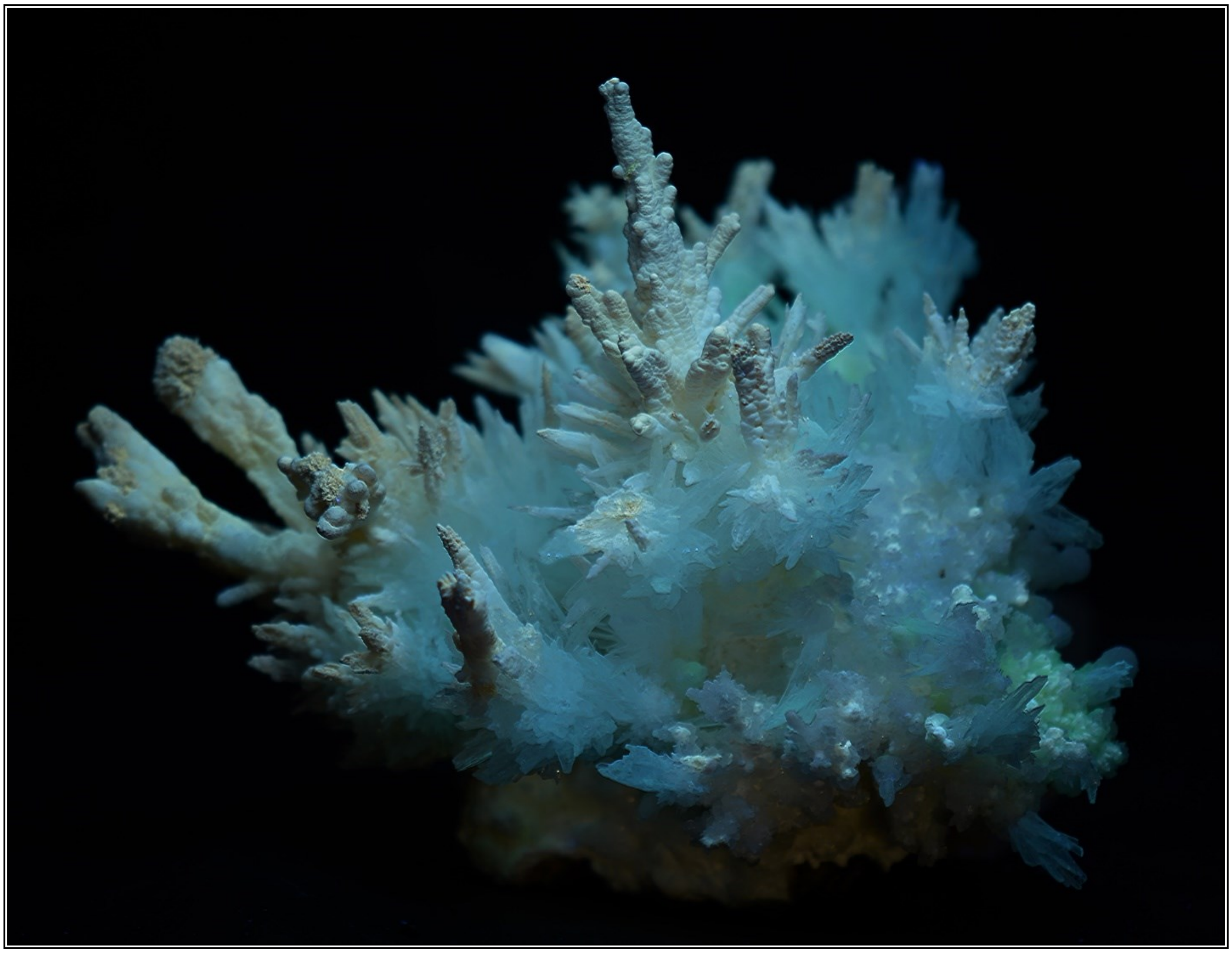
SUMMARY:

The post-mining mineralogy of Bisbee is incomplete, at best. During the operational period of these wonderful mines, few took the time to look at what was so common around them; rather, the focus of the miners and collectors was always on the “Bisbee Classics.” Today, some more than 45 years after the mines closed, most sulfide zones are deep underwater, and the rest of the mine workings are far too dangerous to even consider entering, thus precluding the recovery of new material. Perhaps the Lavender Pit may produce additional specimens, if not new species, but it too is hazardous because of unstable and raveling pit walls.

Yet, in spite of their general unattractiveness and typical instability, some specimens of post-mining minerals were collected during operations. Perhaps upon further examination, these will add to the information base in this neglected aspect of Bisbee's mineralogy.

Post-mining aragonite coating a one-gallon bucket on the 6th level of the Southwest Mine 75 years after it was left when this part of the mine was closed. Note the waterdrop splash crown.

THE FLUORESCENT MINERALS OF BISBEE, AN OVERVIEW:



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. Graeme collection.

The often-spectacular fluorescence and the wide distribution of fluorescent minerals in the mines at Bisbee are not widely 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 of hypogene calcite, where the presence of divalent manganese is only evident by its vivid fluorescence, yet it is abundant and widely distributed. Manganese was incorporated in varying amounts to much of the hydrothermal calcite during mineralization and parts of the Martin limestone during hydrothermal alteration. Such manganoan calcite was literally everywhere as the source of fluorescence in the calcite cementing limestone breccia and partially altered limestone beds, as shown below.

Hydrothermal calcite cementing a limestone breccia under normal light and shortwave light, 3rd level, Southwest Mine, specimen - 13 cm. Graeme collection.

Only 15 of the 337 + recognized species from Bisbee exhibit fluorescence. The color range and intensity are often remarkable. The species from the District that are known to exhibit fluorescence are listed below.

aragonite	fluorite	*meionite*	scheelite
calcite	gypsum	opal	*sphalerite*
cerussite	hemimorphite	powellite	uranopilite
dolomite	hydrozincite	quartz	willemite

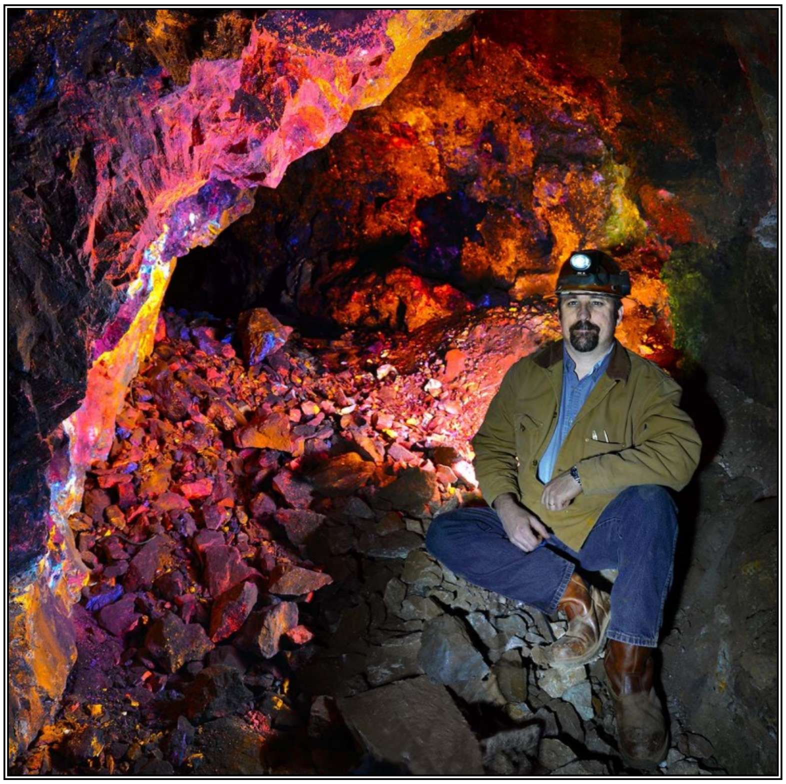
Table 11: Fluorescent minerals recognized at Bisbee, those in italics respond under both SW and LW light.

Hydrothermally altered Martin limestone and hydrothermal calcite, both fluorescing reds, with minor surficial supergene calcite, fluorescing green, under shortwave 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. Graeme/Larkin collection.

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) and are undoubtedly responsible for much of the green responses noted. Wallace (1956) wrote that uranium was so common with the sulfide replacement deposits that he could map the deposits by using the radioactive levels.

Supergene ores were nearly equally radioactive. Underground radiation measurements made by the authors in totally oxidized zones 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.



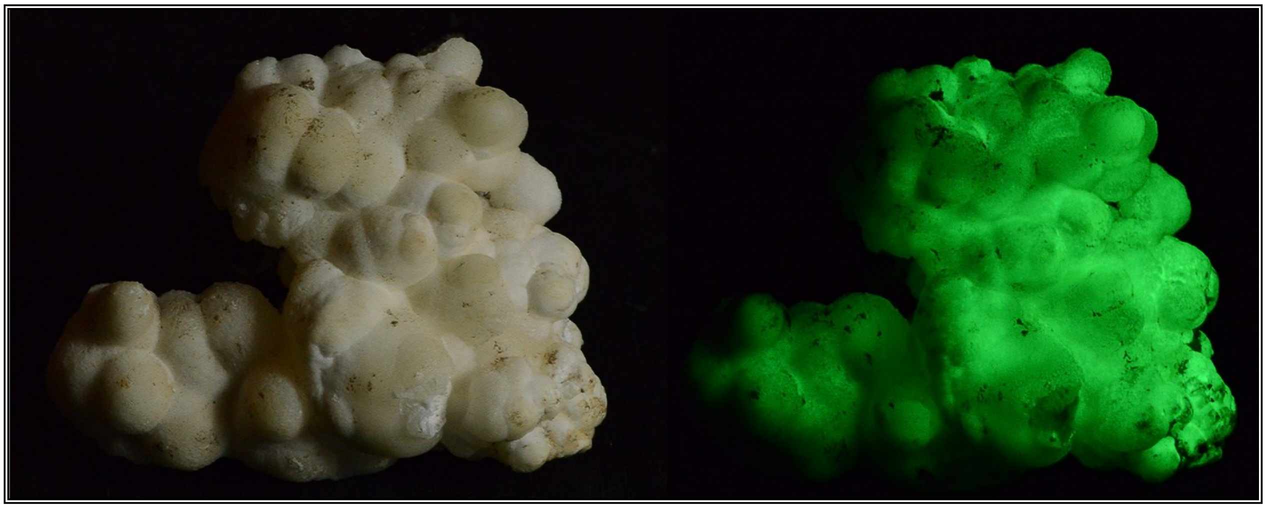
A highly fluorescent area on the "B" level, Copper Queen Mine with sphalerite and hypogene calcite responding to a long-exposure of shortwave ultraviolet light. The photo is a merge of two images to include the left side, with one of the authors (DLG) in the same place, in both. No other photo editing applications used. Graeme/Larkin

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 the "B" level of the Copper Queen Mine, figured above. It is a zone of hydrothermally altered limestone with abundant hydrothermal calcite, highly fluorescent sphalerite, and spotty supergene hydrozincite on some of the post-mining oxidized surfaces. While somewhat limited in size, it is striking in appearance.

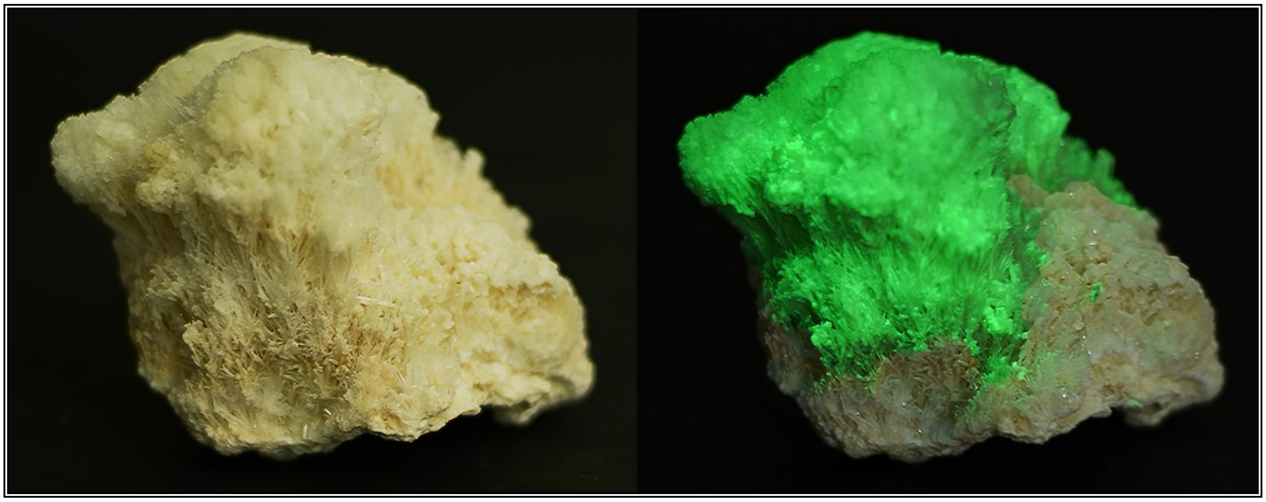
To be sure, information on the distribution of fluorescent minerals in the District, as noted herein, is limited by the access to only a small fraction of those areas mined. Thus, this review cannot be considered as comprehensive. A brief discussion of the fluorescence of those species that are the most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

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, little was fluorescent.



Botryoidal aragonite, right under shortwave light, 6th level, Southwest Mine, specimen-7 cm. Graeme collection.



Aragonite on botryoidal calcite, from a small oxidation cave on the 6th level of the Southwest Mine, specimen- 6.5 cm. right - under shortwave light, left under white light. Graeme collection.

The most impressive fluorescent speleothem material found was from a small, very ordinary oxidation cave on the 6th level of the Southwest Mine. This material fluoresces a vivid, almost emerald green, as shown above. The aragonite occurs as either botryoidal masses or intergrowths of acicular crystals to 5 cm on non-fluorescent botryoidal calcite. This material was locally abundant but decidedly unattractive as a mineral specimen, so very little was collected. Aragonite from several other localities will fluoresce a light yellow-green, as well, but not with this intensity.

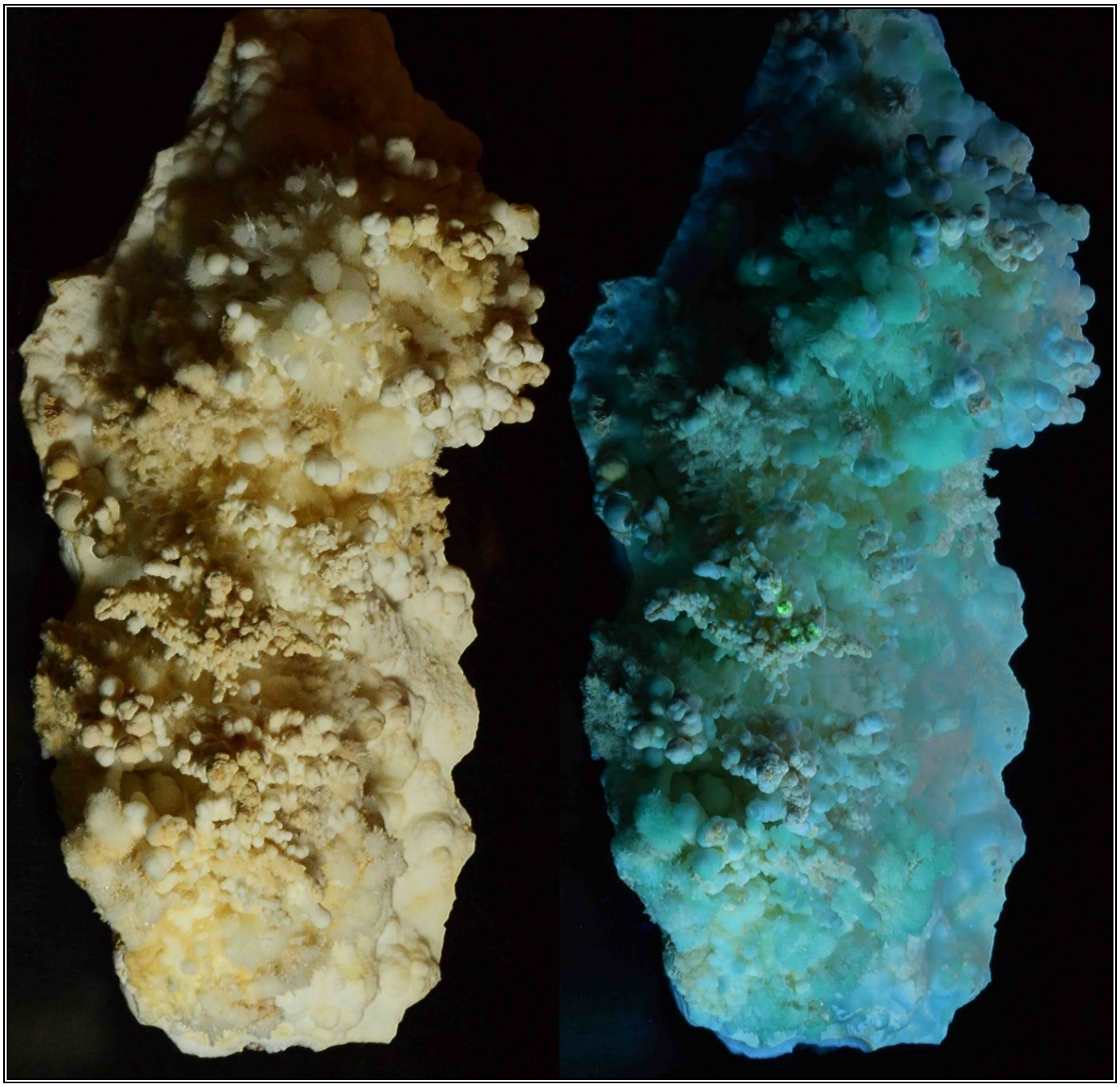
A much larger, well-decorated oxidation cave on the 7th level of this same mine yielded a number of exceptionally fine, white to colorless, aragonite specimens of chisel-like crystals to 5 cm, which fluoresces a lovely light blue under SW and a red/light-purple under LW as shown in several images below. Minor, non-fluorescent dolomite was coating part of the aragonite. A similar light blue response to SW (shortwave) UV light was seen in otherwise rather unattractive specimens of botryoidal aragonite from yet another oxidation cave in this most prolific mine.

White to colorless, aragonite crystals with minor tan dolomite, left - under white light, center - under shortwave light, right – under longwave light, 7th level, Southwest Mine, specimen- 20 cm. Graeme collection.

White to colorless, aragonite crystals with minor tan dolomite, on non-fluorescent botryoidal calcite, right - under shortwave light gives a pale-blueish response, 7th level, Southwest Mine, specimen-3 cm tall. Graeme collection.

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 copper-tinted speleothems, in the many, many oxidation caves and as pockets of well-formed crystals in and adjacent to the oxide ores, few of which were fluorescent.

In 1941, geologists were looking into using fluorescent calcite as an aid in searching for lead/zinc ores, as seen in the Pilares mine of Phelps Dodge in Sonora. Letters to George Schwartz from Carl Trischka, Chief Geologist, in which he discusses trials. However, the lack



Botryoidal aragonite with very minor calcite, right - under shortwave light. The calcite fluoresces a pale green, the aragonite light blue, 6th level, Southwest Mine, specimen - 17 cm. Graeme collection.

of a strong correlation between highly fluorescent calcite and ores, such as seen in Pilares was not consistent enough at Bisbee to inspire continued study.

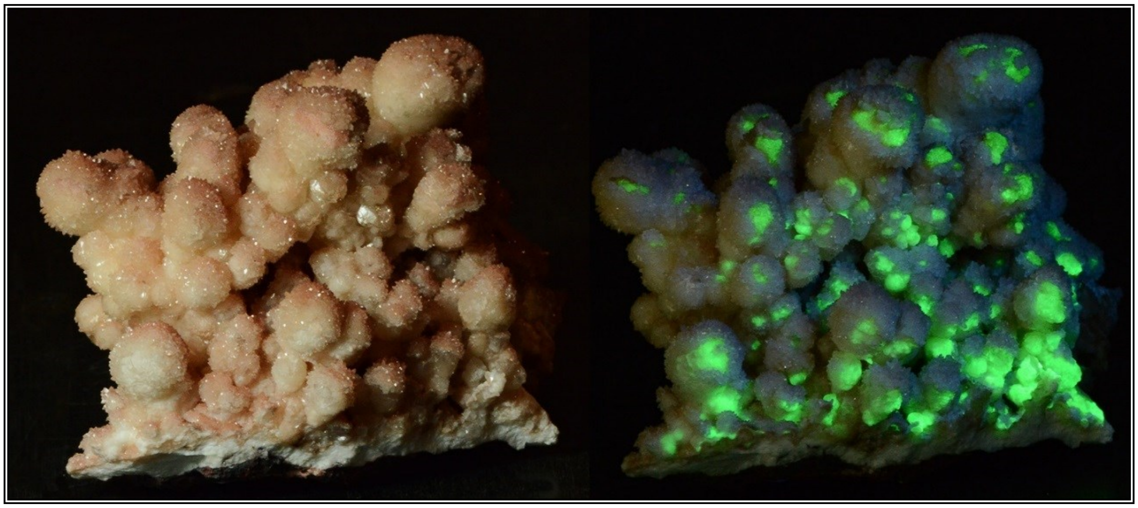
Supergene calcite is pervasive in the oxidized zones, which compose nearly half of the mineralized material mined underground. Several depositional environments for supergene calcite are common, with each variation presenting generally differing fluorescence if present. Multiple depositional periods are a characteristic of most calcites from the supergene environments, as it was a continuing process over time, often extended periods, and under both subaerial and subaqueous situations.

Cave speleothems were everywhere in the ubiquitous caves and large voids, which were common in the totally oxidized zones of the western part of the district (Graeme et al., 2016b). These are largely subaerial in the deposition, but subaqueous crystals formed in subsequently flooded areas, often coating the earlier speleothems. A layered mixture of non-fluorescent calcite with fluorescent relic solution lines were present, reflecting either more than one flooding event or fluctuating levels of a single event over time. Fluorescent calcite reflecting differing solutions is relatively common, under short wave light, as a partial fluorescence.

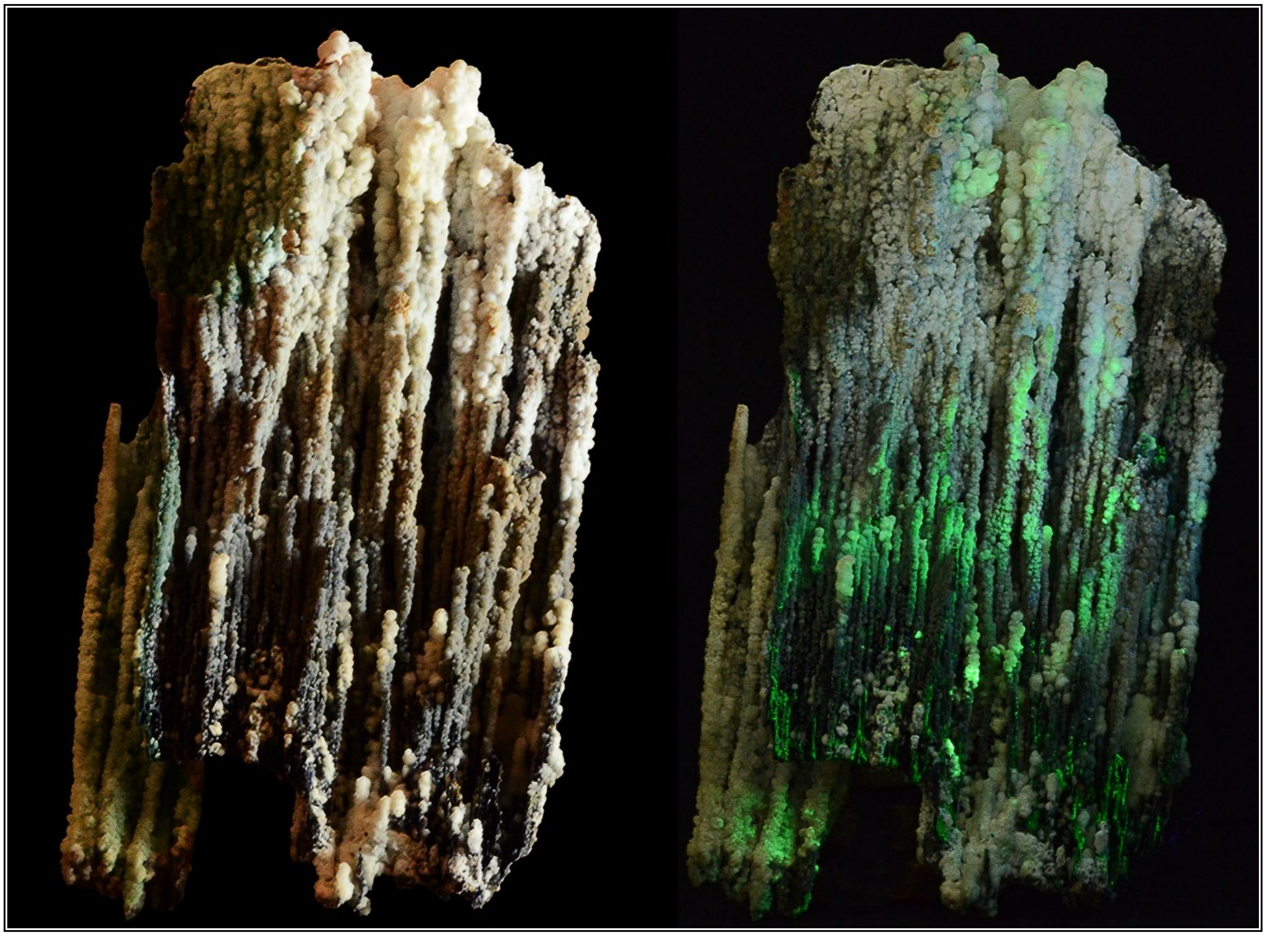
When fluorescent and under SW light, these speleothems usually respond with varying tones of yellow-green. However, other responses have been observed on rare occasions. Longwave light rarely elicits any response.

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 degrees of copper/iron tinting so commonly seen 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 of historic solution levels.

Botryoidal calcite from an oxidation cave, 6th level, Southwest Mine, specimen - 8.7 cm. Graeme collection.



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

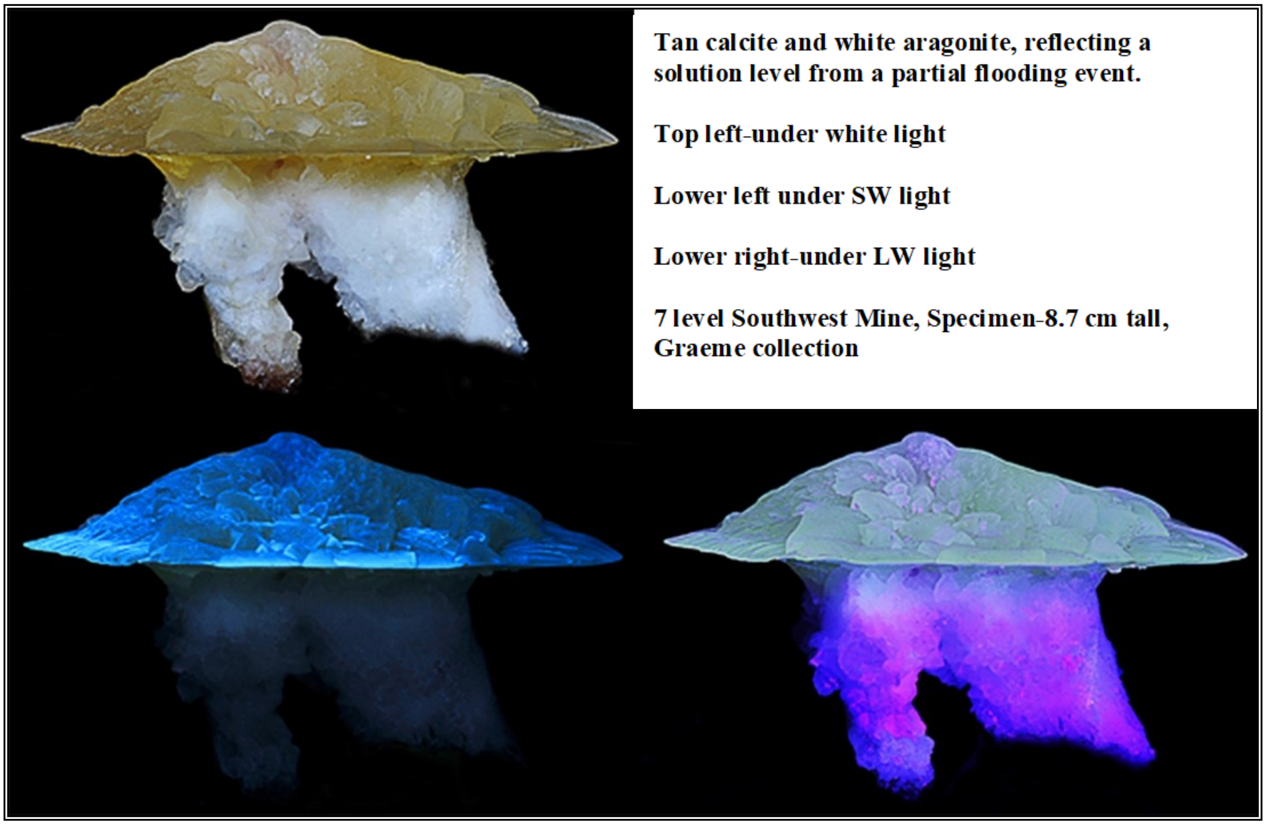


Botryoidal calcite with partial fluorescence, coating stalactitic goethite, 6th level, Southwest Mine; left under white light, right - under shortwave light, specimen - 17.3 cm high. It is highly probable that the fluorescent material reflects a late-stage deposition episode, which chemically varied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

Supergene calcite from the oxidation caves, which formed under subaqueous conditions responds differently, when fluorescent. Often, several relic solution lines were present, reflecting either more than one flooding event or fluctuating levels of a single event over time. Speleothem coloring and a wide range of supergene minerals in the caves reflect that varied solution chemistry entered these openings was common.

Supergene calcite from the oxidation caves, which formed under subaqueous conditions responds differently, when fluorescent. Often, several relic solution lines were present, reflecting either more than one flooding event or fluctuating levels of a single event over time.

The common flooding of these openings over geologic time left calcite growth, usually crystals, at the solution level, developing a horizontal line of crystals at the solution level. Commonly, the subaqueous calcite from caves responds blue-white under short wave light and a curious greenish hue under longwave light. The longwave response is not universal but is more common than short wave fluorescence.



Tan calcite and white aragonite, reflecting a solution level from a partial flooding event.

Top left-under white light

Lower left under SW light

Lower right-under LW light

7 level Southwest Mine, Specimen-8.7 cm tall, Graeme collection

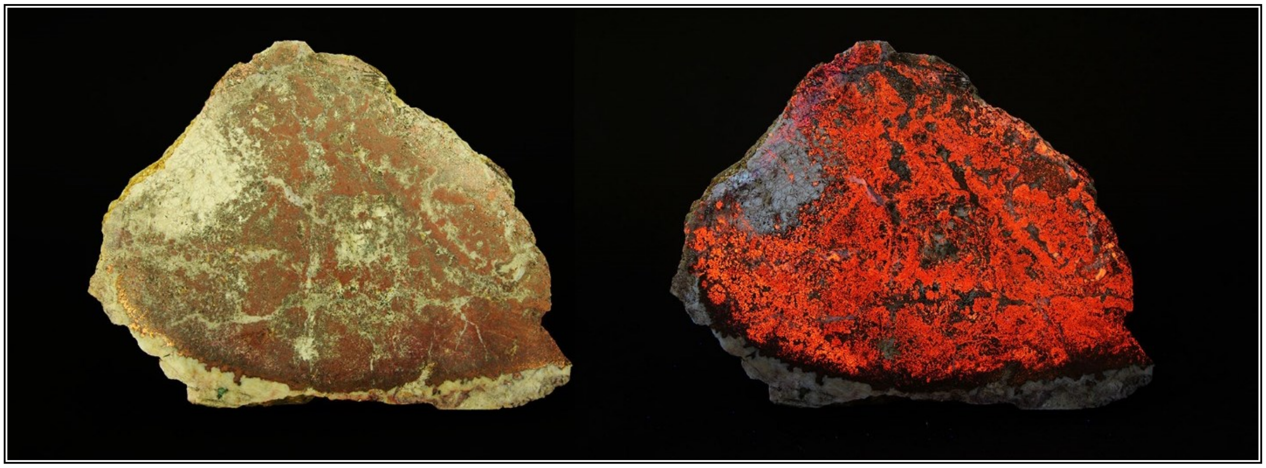
In the ores, calcite was often associated with copper minerals such as malachite, copper, and cuprite, yielding spectacular, classic mineral specimens, almost all of which are not fluorescent. Perhaps fluorescence was quenched by included metals.

Though abundant and pervasive, limited amounts of supergene calcite fluoresce under short wave light and even less under longwave light. Voids with supergene calcite in and adjacent to the many oxide orebodies were everywhere. For the most part, however, the calcite found in these vugs was not anything significant from a specimen standpoint unless brightly colored and even less impressive as fluorescent specimens.

This study has shown that very little supergene calcite associated with the oxide ores is fluorescent, something of a surprise. An example of a reasonably typical oxide ore mass with colorless to white calcite and malachite lining voids in goethite is shown below.

Calcite with malachite lining voids in oxide ore. View – 1 .5 meters. 5th level of the Southwest Mine. Graeme/Larkin collection

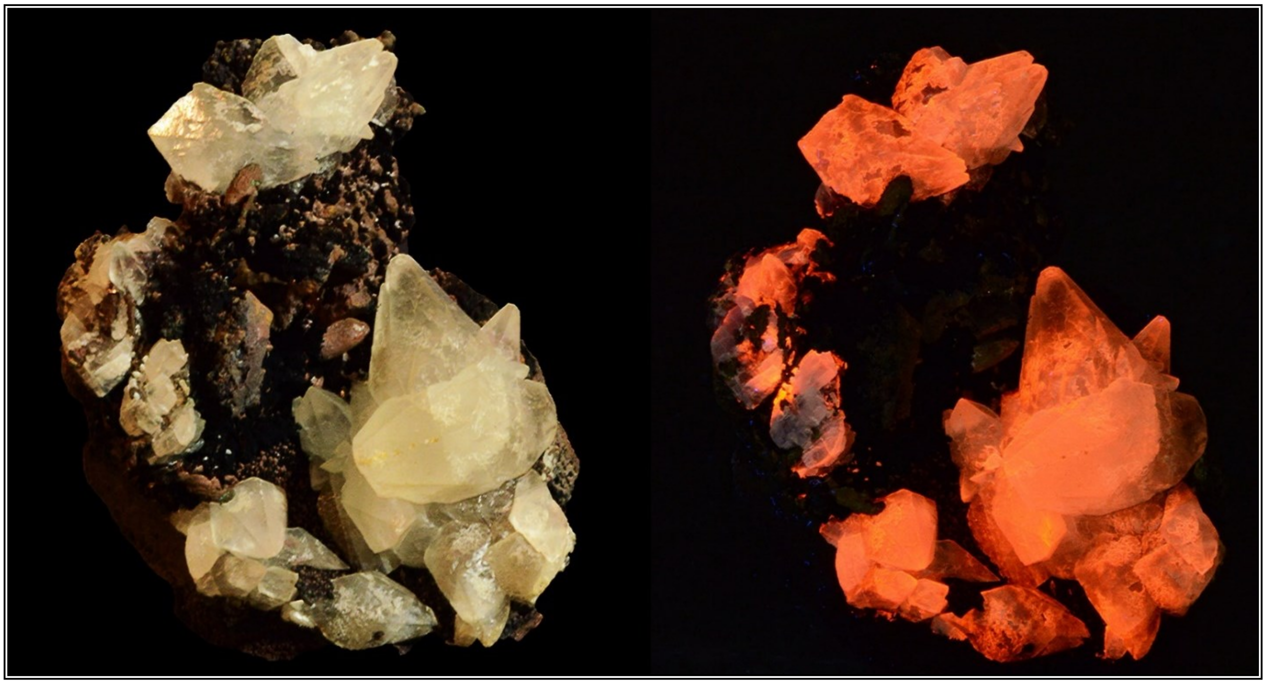
There is one remarkable exception, that is, a consistent, strong red-red/orange response of calcite associated with native copper that is clearly supergene in origin. The several dozen specimens in our collection of calcites associated with copper **all** fluoresce a remarkable bright red/orange to red under shortwave. Typically, the copper was paragenetically earlier, with some of it penny-bright and unoxidized included in calcite. Any copper which was not protected by calcite invariably had the typical patina from oxidation.



A large chunk of supergene calcite completely encasing spongy copper with quartz under shortwave light with polished face, 1900 level, Campbell Mine, specimen - 17 cm. Graeme collection.

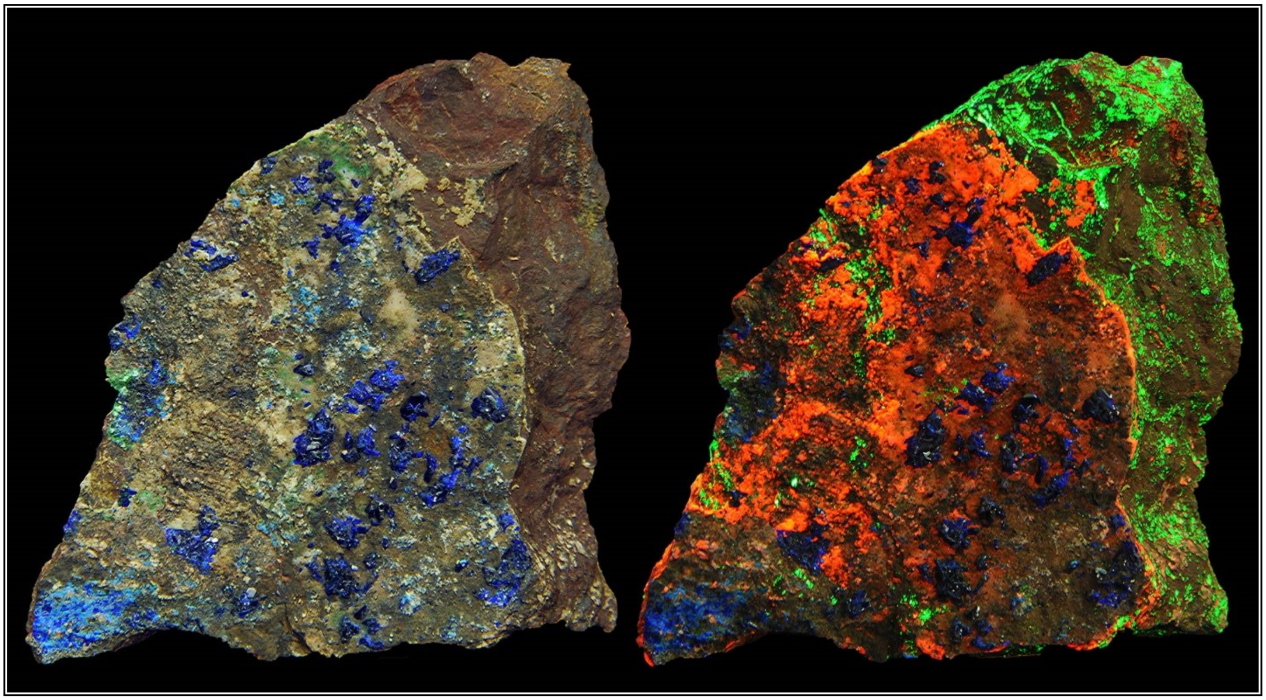
Locally, this material is often called "campbellite" when more cuprite and/or malachite is present. It is often used for jewelry-making as the cut stones are quite nice.

Surprisingly, for longwave light, however, with little if any response. The presence of other species, such as cuprite or malachite, does not appear to affect this strong fluorescence. All the calcite is supergene in origin; thus, the response cannot be attributed to the mangano effect seen in hydrothermal calcite. Specimens of copper and calcite from the Campbell, Cole, Czar, and Hoatson mines are the most common of this type. The reason for the invariably red–red/orange fluorescence of calcite when elemental copper is, at present unclear.



Supergene calcite as crystals to 2.2 cm with copper on goethite under shortwave light, Czar Mine, specimen - 6.8cm. Graeme collection.

Calcite with fine copper spinel-twinned crystals on goethite under shortwave light, 26–K stope, 1300 level, Cole Mine, specimen - 11cm. Graeme collection.



Supergene calcite fluorescing red/orange with non-fluorescent azurite on a mixture of willemite (strong green) and non-flourescent manganese oxides under short wave light. Substantial native copper was associated with the rich ores in this stope, which may account for the red response in calcite, as is invariably seen with Bisbee copper/calcite combinations. However, no copper is evident in this specimen. Cuprite stope, Tunnel level, Higgins Mine, specimen – 6.5 cm. Graeme collection.

Hypogene calcite is widely distributed and abundant as both the localized, hypogene alteration of carbonate rock units and as hydrothermally deposited crystals lining hydrothermally developed voids. The alteration of the limestone appears to have occurred during mineralization. There are no visual clues for recognizing the altered limestone without UV light.

Somewhat corroded, hydrothermal calcite with minor amethystine quartz and malachite-coated chalcopyrite under white (left) and shortwave light (right), 2700 level, Campbell Mine, view – 5.2 cm. Graeme collection.

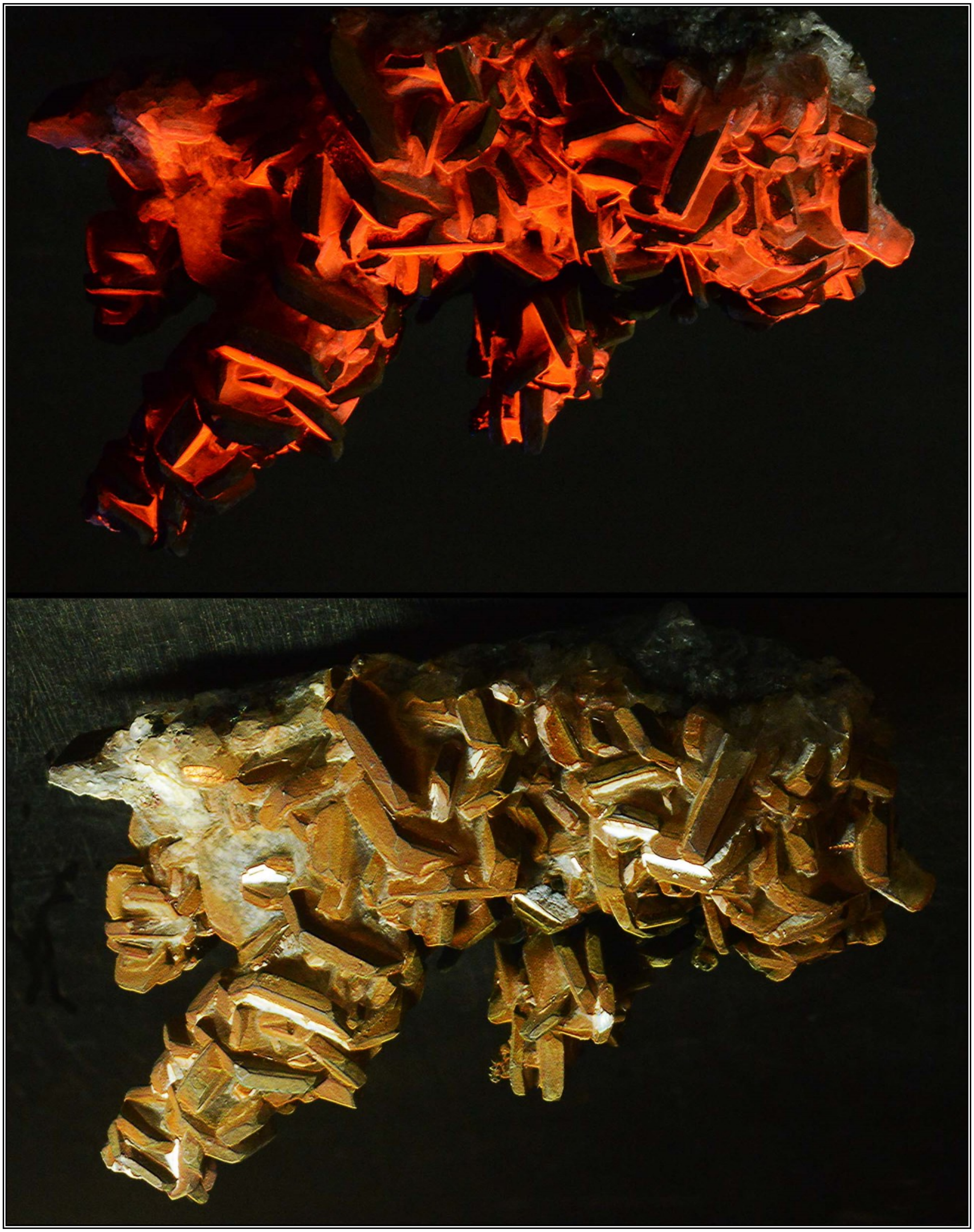
The malachite is probably post-mining in origin, as a surficial alteration of chalcopyrite from exposure to the elements, given that it was in a garden for several decades; a common fate for many Bisbee calcite specimens.

The hosting limestones at Bisbee were tight, with very few openings. The sulfide replacement deposits were very much the same, which accounts for the general lack of sulfide mineral crystals in the hypogene ores. Late-stage hydrothermal voids were developed as few and small openings of a post-mineralization stage near the orebodies. These voids were often partially lined by calcite forms and, on rare occasions, a few minor sulfides, along with amethyst in varying quantities. Corrosion of the calcite to differing degrees is evident. Invariably, the calcite is highly fluorescent. A good example is shown above.

Somewhat distant from the orebodies, even beyond the distal lead-zinc deposits, large hydrothermal voids were etched out of the limestone. These were formed in the deeper parts of the Campbell, Junction, and Denn mines in altered host rocks. All voids were utterly devoid of sulfide minerals but were often lined with complex calcite crystals, all of the same forms in each individual pocket. Minor goethite and manganese oxides were frequently present as coatings, both of the void walls, and as a crust or thin, external coating or inclusions in the calcite crystals.

Hydrothermal calcite with minor unidentified manganese oxide as matrix and as light phantom inclusions, under white light (left) and under shortwave light (right), 2566 level, Campbell Mine, Specimen - 6 cm. Graeme collection.

Hydrothermal calcite under white light–left, under shortwave light–center and under longwave light at the right. Specimen 11.4 cm, from the Junction Mine. Graeme collection.



Hydrothermal calcite which has overgrown goethite stalactites. The non-vertical orientation, is how it was oriented when collected, reflecting a pre-tilting deposition. It is partially coated by later goethite, which in turn, is partially overgrown by a later generation of white to colorless, hydrothermal calcite. Under shortwave light, from the 2566 level Campbell Mine, Specimen – 8.2 cm. Graeme collection.

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, as the Resident Geologist at the Copper Queen Branch. It became evident that these hydrothermal pockets were formed and crystal-lined after mineralization, as manifested by the total lack of sulfides or evidence of sulfides ever having been present.

Several pockets in the deeper workings of the Campbell Mine contained goethite as an open space lining and/or coating of calcite crystals. The most impressive was goethite as stalactitic forms to 10 cm of pre-tilting or pre-Laramide orogeny, upon which fine two cm hexagonal calcite crystals were randomly deposited. 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 molds of removed pyrite and staining caused by mobilization of iron were both absent in the encasing limestone.

The premier locality for highly fluorescent hypogene calcite at Bisbee has to be the hydrothermal calcite from several large voids on and above the 2566 level of the Campbell Mine. While several locations on and above this level produced fine examples, as shown above, one site was outstanding. Calcite occurred as randomly oriented, hexagonal crystals to 2 cm and typically with a coating of goethite that yields a bright red fluorescence under shortwave light but a much more muted one to longwave. 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.

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 tough 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 of specimens collected are free of significant damage to make collector quality specimens by today's standards, but their brilliant and contrasting fluorescence still remains.

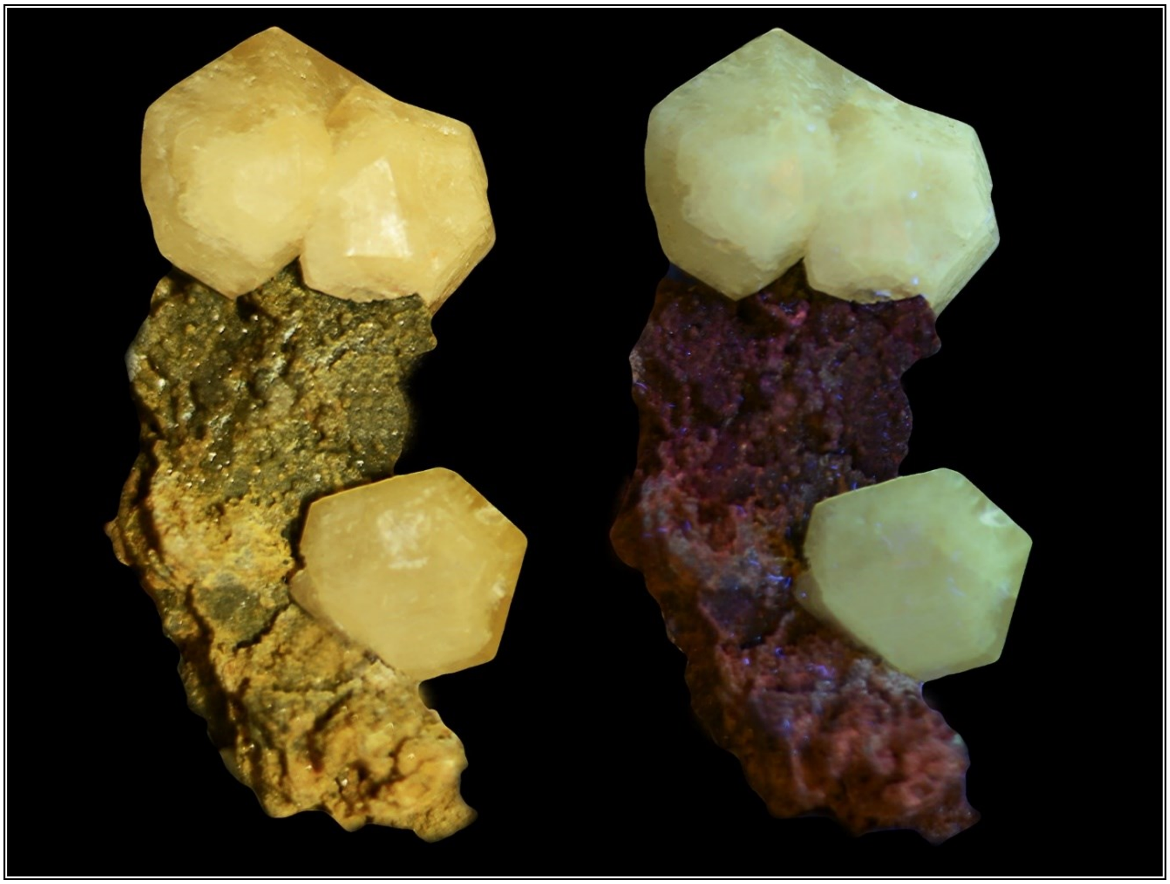
Crystalline hypogene calcite in the western part of the mineralized area was relatively uncommon and the very few hypogene developed-voids recognized have been impacted by supergene alteration to the point of being unrecognized, as such.

Right: Siderite as epimorph-type pseudomorphs after hypogene calcite. Holbrook Extension, Lavender Pit Mine, view - 4.9 cm. Graeme collection

Almost all of the hypogene calcite they contained appears to have been either replaced or overgrown by later supergene calcite. It was common for the calcite to be replaced by other secondary minerals such as siderite or goethite (Graeme et al. 2016b), as numerous epimorphs of these iron minerals after calcite have been found.

Cerussite: Cerussite was a common ore mineral in the western, oxidized part of the district. Some orebodies contained 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.

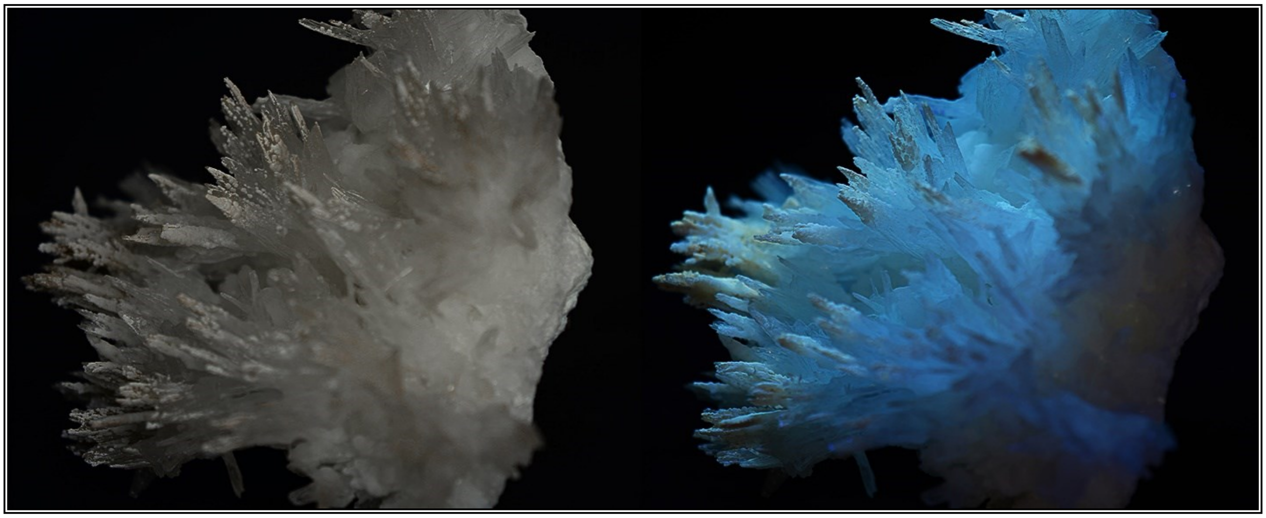
However, fluorescent cerussite appears to be relatively uncommon, if not rare. More than two dozen Bisbee cerussite specimens in our collection were checked for fluorescence under both short wave and longwave, but only the one illustrated below responded to UV light, with a near-white color under shortwave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



Cerussite on smithsonite and goethite under shortwave light (right), Gardner Mine, specimen - 7.1 cm. Graeme collection.

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 tests 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 short wave and longwave light. However, in general, supergene dolomite was rarely fluorescent, even mildly.



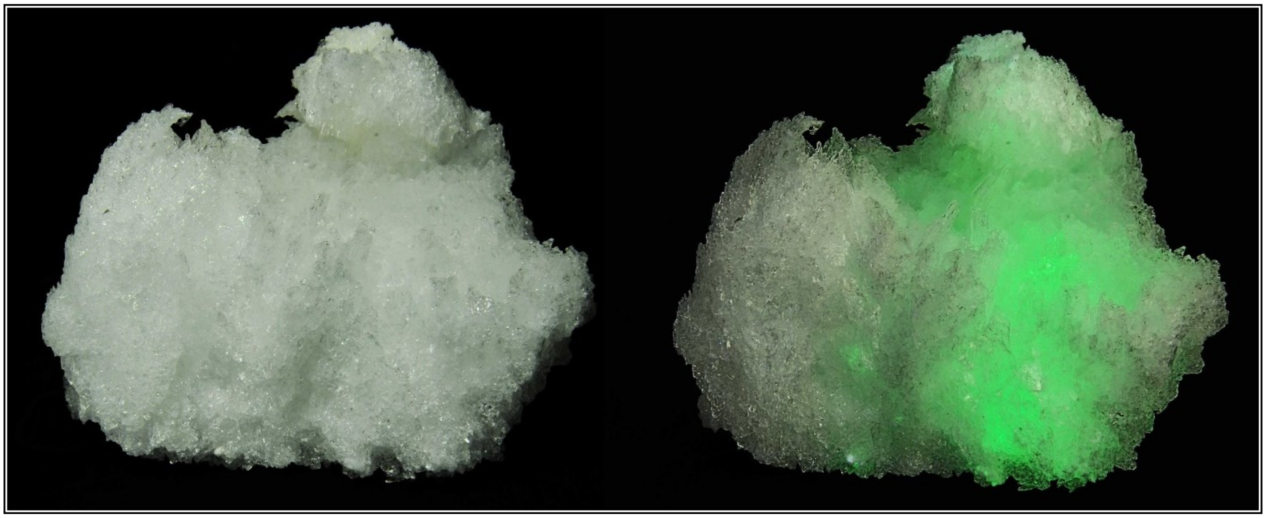
White to cream-colored fluorescing dolomite on the tips of superb, light-blue fluorescing aragonite crystals to 3.5 cm, under shortwave light 7h level, Southwest Mine. Graeme collection.

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

Gypsum: Supergene gypsum was most common in many oxidation caves but never abundant. It occurred as the classic rams-horn growths and coatings over calcite and in one case as feather-light blocks to 50 centimeters made of small, thin crystals were found in the bottom of a small oxidation cave with an unusual amount of gypsum.

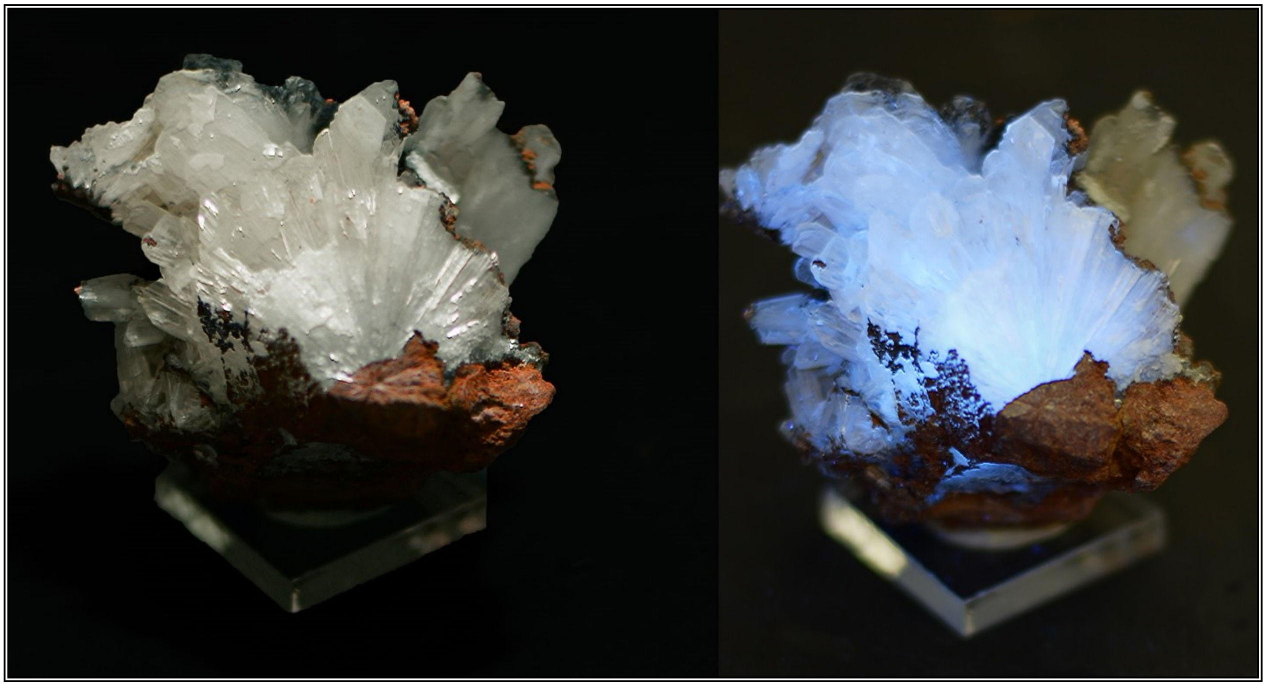
Fluorescent gypsum has been noted in just two of the many caves. This probably does not truly reflect its actual distribution because access to most caves is often impossible, as the ground has caved and/or they were backfilled for safety reasons. And too, supergene gypsum at Bisbee was uncommon and uninspiring at best, thus very little was collected.

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.



Partially fluorescent gypsum under shortwave light, with very minor flecks of included malachite 6th level, Southwest Mine, specimen - 9 cm. Graeme collection.

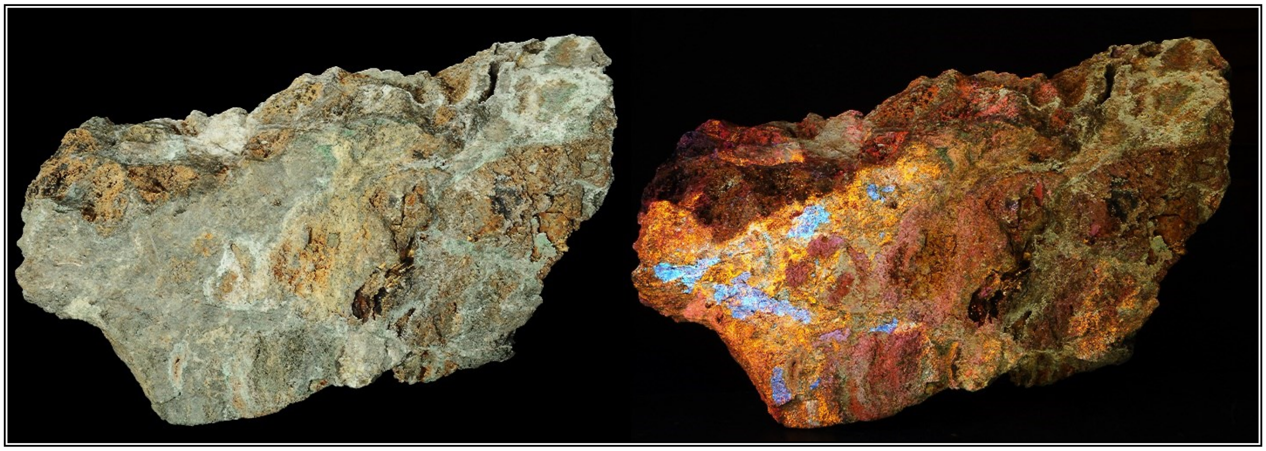
Hemimorphite: Hemimorphite is one of the few common supergene silicate minerals at Bisbee, but very little was fluorescent, and that was under SW light only. A limited number of specimens from Cole and the Copper Queen mines exhibit partial fluorescence. The many specimens checked from other mines and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



Bright-white partial fluorescing hemimorphite on hematite with Chalcophanite under shortwave light, 26 K stope, 1200 level, Cole Mine, specimen – 3.6 cm. Graeme collection.

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.

Post-mining hydrozincite was common wherever 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.



Hydrozincite fluorescing blue-white color. With sphalerite (orange fluorescence), calcite is fluorescing (red) under shortwave light. Specimen - 15.4 kg and 33 cm in length. "B" level of the Copper Queen Mine below. Graeme collection.

Meionite: A light, bluish-white response under shortwave light is typical. The grain size may lighten the color. While relatively abundant as microscopic specks as a minor component of hydrothermal gangue, pieces of any size are uncommon. Large pieces of compact slender prismatic crystals were found between the Junction Mine and the intrusive as almost vein-like streaks in intensely altered limestone.

Opal: Opal has been found in several areas in the mines as a late-stage mineral. Common 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 shortwave ultraviolet light, most of this opal was green in fluorescence, while some were cream-colored.

Along the fringes of a largely collapsed stope above the 100 level of the Higgins Mine were pockets of calcite, several of which had spotty, partial coatings of 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. It is highly green fluorescent under short wave ultraviolet light.

Powellite: Powellite gives cream to yellow response to shortwave light. It 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, primarily 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 shortwave ultraviolet 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 expected bright blue-white response under short wave ultraviolet light. However, it does not respond to longwave ultraviolet light. Scheelite is also a common but very minor accessory mineral in the chalcopyrite type ores, as described by Schumer (2017). However, because of the tiny amounts in each occurrence, its fluorescence is not often apparent.

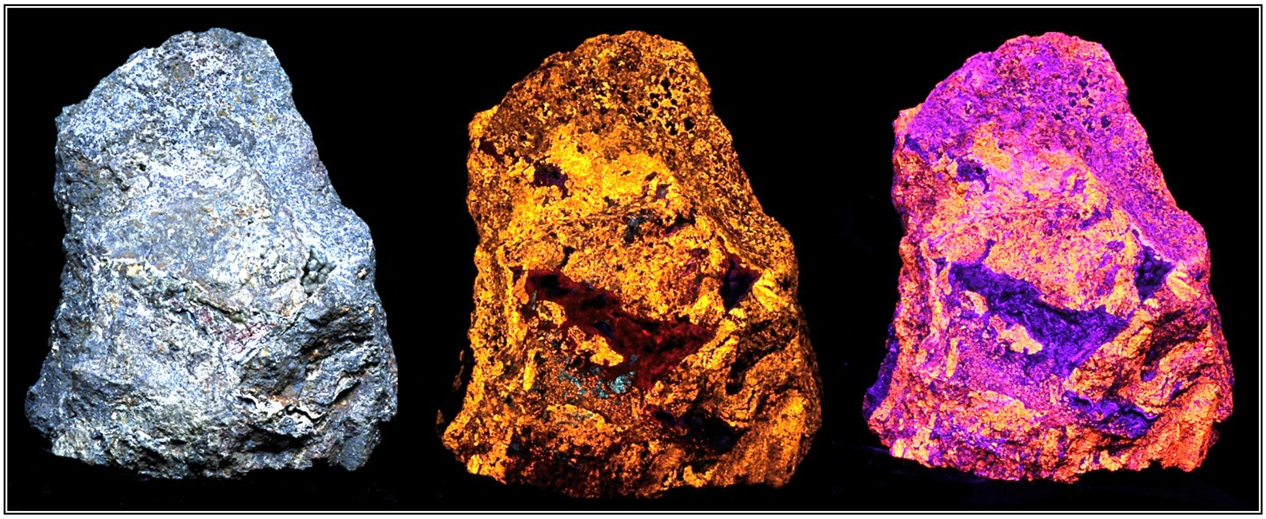
Blue-white fluorescing scheelite in quartz with minor black chalcocite and cuprotungstite under shortwave light, from a mineralized quartz outcrop near the Portage Lake Mine, specimen – 20 cm. Graeme collection.

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 glowed when struck with steel tools. Some color variation has been noted in fluorescent sphalerite, but far and away, orange is the dominant response.

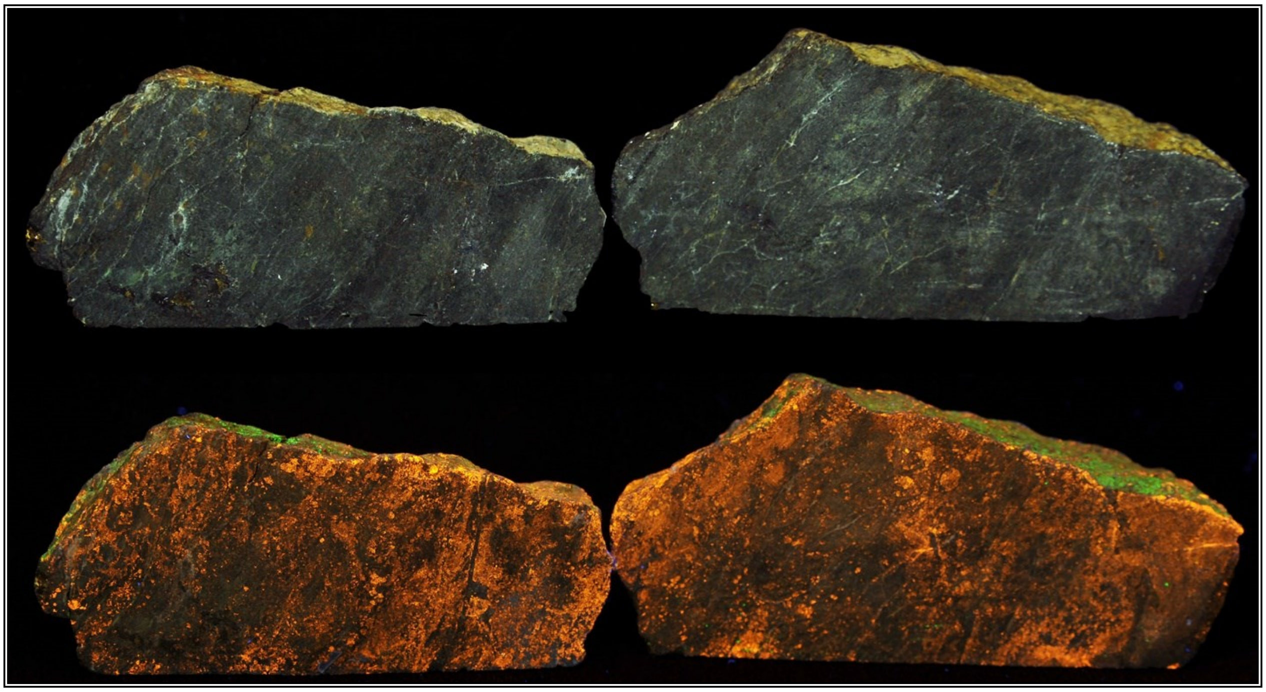
A small ore pod of perhaps several hundred tons with partially oxidized sphalerite above the "B" level of the Copper Queen Mine contained some of the most vividly fluorescent sphalerite under short-wave and longwave ultraviolet light at Bisbee. It was associated with equally fluorescent calcite and minor post-mining hydrozincite, as shown below. 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 treat. It was not uncommon to hit small pods of lead/zinc mineralization and leave them in place. Their presence was noted in company reports and marked on maps so that if and when mining these minerals in their form (supergene vs. hypogene) became economical, the occurrence will be available.

Post-mining 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 shortwave light. One of the authors, RWG IV is in the photo on "B" level of the Copper Queen Mine. Graeme/Larkin collection.

The Junction mine produced much more sphalerite that was fluorescent than any of the other mines. Much of it was compact, fine-grained, iron-rich sphalerite that gave a bright orange response to shortwave ultraviolet light. Only a relatively small number of these otherwise nondescript specimens were saved. Examples from three separate and distant occurrences in this expansive mine are presented below under short wave light. Interestingly, these and other sphalerite specimens from these mines responded weakly, if at all, to longwave.



Sphalerite, with minor calcite and smithsonite. Left - under white light, center - under shortwave light, right - under longwave light, "B" level, Copper Queen Mine, specimen – 9 cm. Graeme collection.

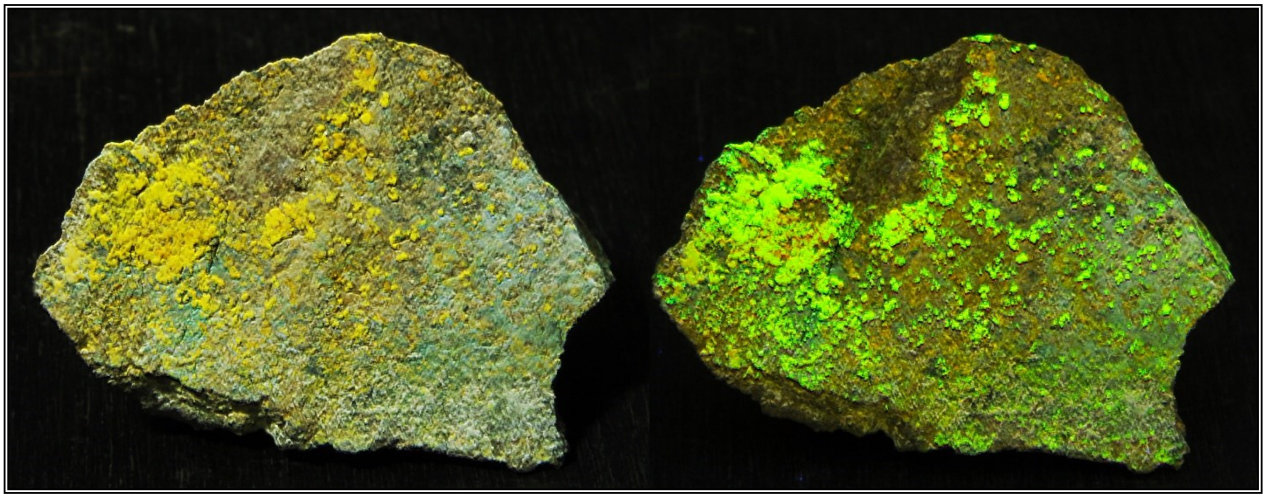


Extremely fine-grained mass of sphalerite, which has been cut and polished for study under shortwave light. The near-parallel orientation of the sphalerite may well be relic textures of the replaced limestone. Junction Mine, specimens-5.5 cm. Graeme collection.

Sphalerite under shortwave light, Junction Mine, specimen-9 cm. Graeme collection.

Sphalerite fluorescing a yellow/orange hue under shortwave light. Note the non-fluorescing pyrite present at the top left. Specimen from the Junction Mine, size –4 cm. Graeme collection.

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.



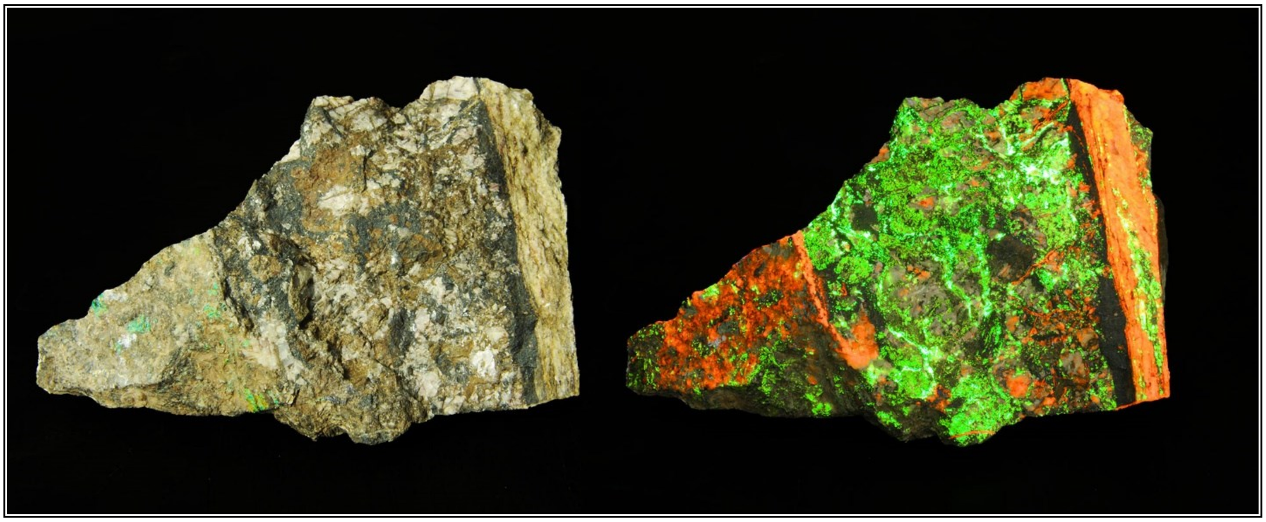
Green fluorescing uranopilite with minor zippeite on pyritic limestone under shortwave light, Cole Mine, specimen–4.5 cm. Graeme collection.

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

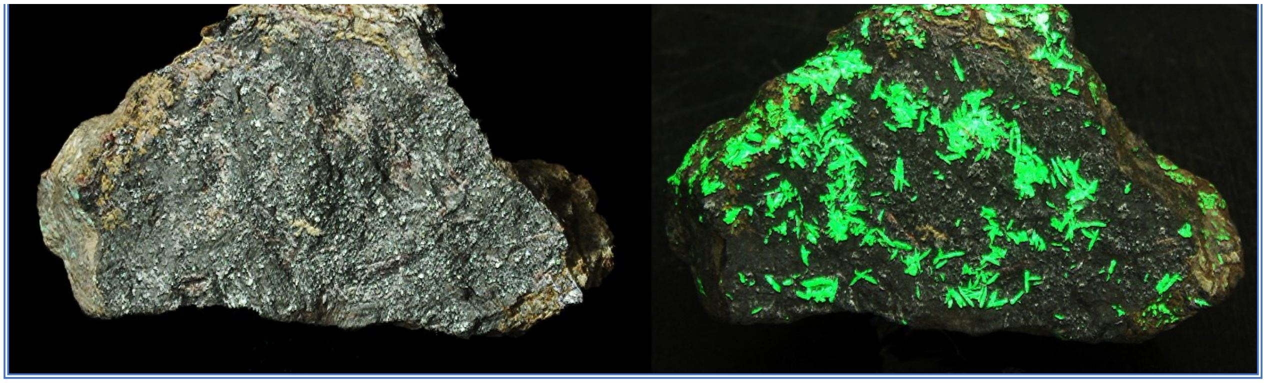
The abundant willemite found in the Cuprite Stope on the Tunnel level of the Higgins mine is strongly phosphorescent. After the short-wave ultraviolet light source is removed, the willemite will continue to glow strongly, slowly diminishing until completion extinction, some 20+

seconds later. This material is the only significantly, phosphorescent material recognized during this study.

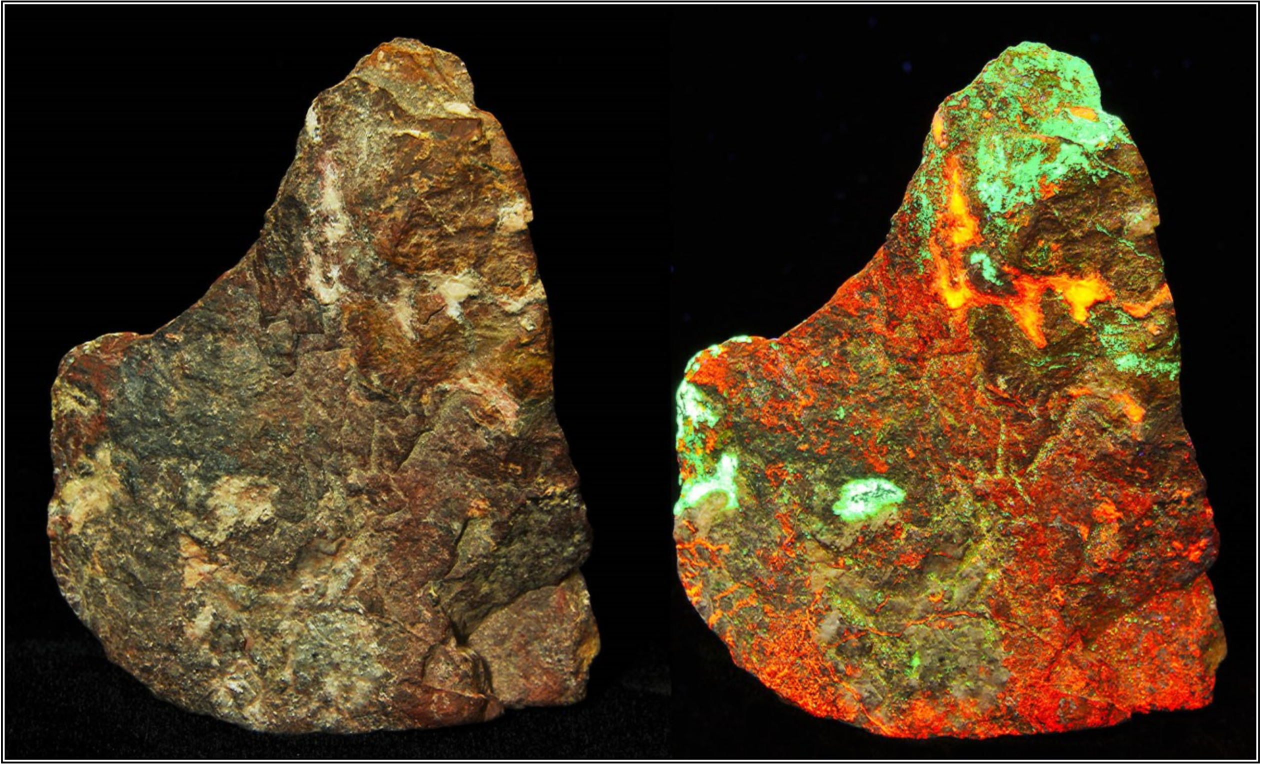
During the late 1940s, highly fluorescent willemite was recognized with lead/zinc ores in the Campbell Mine. Several miners collected the material to sell to the mineral dealers who frequently passed through Bisbee (Melvin Elkins, personal communication, 2016). Local demand for fluorescent material was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



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



Colorless willemite crystals to 2 mm. on braunite under white light, left and under shortwave light right, “Cuprite” stope, Tunnel level, Higgins Mine. Graeme collection.



Willemite (green) with highly fluorescent, iron-stained calcite (red–red/orange); Left under white light, right under shortwave light, 2100 level, Campbell Mine, specimen-11 cm. Graeme collection.

SUMMARY:

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

For science, it is an essential tool in the study of almost 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 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. 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 and form of fluorescent minerals in multi-mineral specimens is very useful.

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THE AUTHORS

Left to right, Douglas L. Graeme, Richard W. Graeme III, and Richard W. Graeme IV with a very small part of the collection

Bisbee and the Graeme family: Our connection to Bisbee began in 1883, when Charles Keeler came to this young mining camp as a boy, seeking work, which he quickly found in the Copper Queen Mine. For most of the next 62 years, he would call Bisbee his home and mining his trade. He retired in 1945 but continued to live close to the Cole Shaft, where he had spent so many working days. Charles was our grandfather/great-grandfather. It was his many stories and reminisces that kindled a life-long interest within Richard Graeme III for all things Bisbee, most of all the minerals as he was a mineral collector. The legacy of Keeler's interest continues with unabated passion in Richard Graeme IV and Douglas Graeme. Together, we have assembled the largest and most complete collection of Bisbee minerals with some 7,000 specimens. This is supplemented with an extensive research library and a historical photograph collection of more than 6,000 images, all of which provide an unparalleled research basis.

And too, we have spent 10s of thousands of hours in the field, underground, and the laboratory over the last 70 years. The resources and experiences provide a unique platform for the telling of Bisbee's colorful past and its wonderful minerals.

Richard (Dick) W. Graeme III Born in Bisbee, Arizona, in 1941, and was an active collector of Bisbee minerals by the age of six. By his early teens, he had amassed a good collection of minerals and was well known to mineral dealers and other collectors as a source of specimens. In 1959, while looking for minerals in the Cole Mine, he collected a specimen that would later be recognized as a species new to science and which would be named graemite in his honor (Williams and Matter, 1974).

Dick went to work in the mines in 1960 as a laborer where he would remain for the next dozen years, during which he completed a BS in Geological Engineering in 1972 at the University of Arizona. The day after receiving his diploma, he was promoted to Resident Geologist of the Copper Queen Branch. With the closure of the mines, Dick left Bisbee but continued to study its mineralogy, geology, and history while writing about all of these aspects (Graeme, R.W., 1981, 1987, 1993, 1999, 2008, 2012a, 2012b), and (Graeme et al., 2015). After 55 consecutive years in the copper industry, much outside of the U.S. in senior management positions, he retired and lived in Lima, Peru until his death on June 2, 2021.

Richard (Rich) W. Graeme IV: Born in Bisbee, Arizona, in 1968, Rich was collecting underground with his father and twin brother by age six. Minerals and mining were the focal points of his youth, with many hundreds of hours underground in Bisbee and other western mining areas collecting minerals and mining artifacts. In 1986, along with his twin, he collected what is surely Bisbee's finest cuprite specimen along with exceptional examples of some of the rarest of copper minerals.

Rich has worked in the goldfields at Nome, Alaska, underground in the fabled Sunnyside Mine at Silverton, Colorado, and the Continental Mine near Silver City, New Mexico, as well as the Golden Queen Mine near Mojave, California, gaining first-hand experience in underground mining. Later, he worked in Bisbee at the Queen Mine Tours as a guide, where his knowledge base was put to full use.

Because of the difficult times for the domestic mining industry, Rich switched from a mining major to education and received his degree in education from the University of Arizona in1999. He now teaches science in nearby Sierra Vista.

Douglas (Doug) L. Graeme: Born in Bisbee, Arizona in 1968, Doug was underground and collecting minerals and artifacts by the age of six. From that point on, his focus has been on Bisbee, and its incredible mineralogy interspersed with mineral finds elsewhere. Most of his free time as a young boy was spent underground in a usually successful quest for minerals and mining-related memorabilia. The news and significance of his discoveries were shared with fellow collectors when, beginning at age 13, he and his brother made frequent presentations at the New Mexico Mineral Symposium.

While he collected many fine minerals in his teen years, nothing compares to the extraordinary cuprite he collected with his twin in the Southwest Mine. Along with what is one of the world's best cuprites, he also collected a diverse suite of rare and uncommon copper minerals, some of which remain the best examples known for the species.

By the time Doug had completed three years of university studies with a mining major, the U.S. mining industry was well into its decline. Nonetheless, he worked on the surface with the gold dredges of Nome, Alaska, and underground in the specimen-rich Sunnyside Mine near Silverton, Colorado, as well as in the Continental Mine in Fierro, near Silver City, New Mexico. Later he would work at the Queen Mine Tours as a guide then in Kartchner Caverns during its development using his mining experience. Now Doug has returned to work in Bisbee as the Manager for the Queen Mine Tours, where his passion and knowledge help keep the legend of Bisbee alive.

PUBLICATIONS:

Our publications include chapters in various books or periodicals over a 40-year period. More recently, we have taken important segments of Bisbee's geology, mining, and history and published' detailed overviews of these various aspects. All are listed below by year published.

1981 - The *Mineralogical Record,* **12,** 258-319, "Famous mineral localities: Bisbee, Arizona": By
Richard. W. Graeme III

1987 - "Bisbee; Arizona's Dowager Queen of Copper Camps": A look at her first 50 years" (in *History of Arizona Mining*): By Richard. W. Graeme III

1992 – "The Queen and Her Court" in *Bisbee: Urban Outpost on the Frontier*, University of Arizona Press.: By Richard W. Graeme III. 41-55, 144 p.

1993 - *Mineralogical Record,* **24,** 421-436, Bisbee revisited, an update on the mineralogy of this famous locality.: By Richard. W. Graeme III

1999 - *The Mining History Journal* **6** 39-5, The Copper Queen Consolidated Mining Company 1885- 1917, A History of the Company and its Employees**.**, The Mining History Association, Denver, CO.: By Richard. W. Graeme III

2012 - *Mineralogical Record* supplement "Treasures of the Queen." The Bisbee Exposition.: By Richard. W. Graeme III

2012 - Collecting Arizona: State of Mines, Legacy of Minerals 1st Edition: By Tony L. Potucek (Author), Les Presmyk (Author), Richard Graeme (Author), Terry C. Wallace (Editor), Lithographie, LLC, 366 p.

2013 - Bisbee (Postcard History) Arcadia Publishing: By Annie Graeme Larkin. 128 p.

2015a - *Mineralogical Record* **46,** 627-641, An update on the Minerals of Bisbee Cochise County, Arizona.: By R.W. Graeme III, R. W. Graeme IV, and D.L. Graeme.

2015b - Early Bisbee (Images of America) Arcadia Publishing: by Annie Graeme Larkin, Douglas L. Graeme, Richard W. Graeme IV. 129 p.

2016a - *The Forgotten Caves of Bisbee, Arizona.* R.W. Graeme, III, D.L. Graeme, and R.W. Graeme IV, Copper Czar Publishing, Bisbee, Arizona, 175 p.

2016b - *An Overview of the Post- Mining Minerals Found at Bisbee, Arizona.* R.W. Graeme, III, D.L. Graeme, R.W. Graeme, IV, Copper Czar Publishing, Bisbee, Arizona, 36 p.

2016c - *Glossary of Mining and Mining Related Terms as used at Bisbee, Arizona*, R.W. Graeme, III, D.L. Graeme, R.W. Graeme, IV, Copper Czar Publishing, Bisbee, Arizona, 136 p.

2020 - *7---- Bells: Mine Safety & Accidents at Bisbee, Arizona*, Second edition: by Richard William Graeme IV Copper Czar Publishing, Bisbee, Arizona, 589 p.