

**SUPERGENE MINERALOGY AND PROCESSES IN THE
SAN XAVIER MINE AREA—PIMA COUNTY, ARIZONA**

by

L. Clark Arnold

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ABSTRACT

This is a study of the supergene mineralogy of the San Xavier West mine located in the Pima mining district, Pima County, Arizona.

The number and composition of secondary species collected are found to be closely related to the relative amounts of the various primary minerals and to the manner in which they were emplaced in the host rock.

Supergene mineral species were selected that appeared to be in equilibrium with their environment, and certain assumptions are made concerning the stability fields of these minerals.

The equilibrium conditions in most cases can be narrowed and often closely defined by combining the stability fields of several secondary minerals. On this basis, two acid environments and one alkaline environment are found to exist and are separable on the basis of mineralogy. The fields of chalcantite and melanterite define a highly acid environment while those of goslarite and malachite define an environment of lower acidity. The association of calcite, rosasite, hemimorphite, and malachite indicate an alkaline environment.

The acidity of the environments is principally determined by the amount of pyrite present, and pH may be lower than 3 if pyrite is abundant and reactive carbonate material lacking.

Also, knowledge of stability relations allowed the history of enrichment and subsequent oxidation to be followed in a case where a transitional species had been removed from reaction by inclusion with gypsum.

INTRODUCTION

This study of the mineralogy of the San Xavier mine is undertaken in order better to understand the action of supergene processes in an arid environment. From a limited number of primary sulfides in a pyrometasomatic deposit formed in carbonate rock, an interesting and surprisingly extensive suite of secondary copper, iron, and zinc minerals has developed.

Location and History of Mine

The San Xavier mine is 22 miles south of Tucson, Arizona, in the Pima mining district. The mine was known to early settlers in the area, but before 1880 ore was removed only from very shallow workings. The first real development was accomplished by C. P. Sykes who purchased the mine in 1880 and formed the San Xavier Mining and Smelting Co.

Since 1897, the mine has produced somewhat over 700,000 tons of ore averaging 5 percent lead and 11 percent zinc with minor amounts of copper and silver. The geology of the mine is typical of the pyrometasomatic deposits of the district.

Since the organization of the San Xavier Mining and Smelting Co., the mine has changed hands four times. The property, now inactive, is owned by the Banner Mining Co. and is currently under option to the Anaconda Copper Corp.

Geology of the Mine

The present investigation was confined to the surface and underground workings of the western extension of the San Xavier mine.

The San Xavier West, also known as the No. 6 shaft of the San Xavier mine, was apparently constructed as an exploratory effort. The 2-compartment shaft of the extension is approximately half a mile southwest of the main San Xavier workings and reaches a depth of 270 feet.

The 100-foot level, the 150-foot level, and the 270-foot level of the extension are connected to the main San Xavier mine by a sub-level between the 270-foot and 150-foot levels.

The small stopes and scarcity of ore imply that little if any profit resulted from exploration to the southwest.

The mine is located in carbonate rocks thought to be of late Paleozoic (Permian?) age, and the workings tend to follow a limestone-arkose fault contact. The arkose is of probable Cretaceous age. The localization of the ore is controlled by an extremely complex fault system involving at least four sets of fractures and by rather intense garnetization of the carbonate host rock.

Method and Scope of the Study

The present investigation was undertaken in the fall of 1963 and completed the following spring. During this time, the author was a member of a group of students engaged in mapping the surface and workings of the San Xavier West. For the most part, fieldwork was completed in the process of mapping the mine.

Specimens were collected from the mine for examination to determine the minerals present. In some instances, particularly with respect to alteration study, thin sections were made, but in general the mineralogical examination was carried out using a variable power binocular microscope.

Identification of the minerals was accomplished by optical methods, by microchemical tests as described by Short (1940), and by X-ray diffraction.

Because of the importance of identification, two or more tests were conducted on each mineral. Several techniques were used to facilitate X-ray investigation of very small specimens as well as mineral mixtures because the quantities of minerals involved were often quite small.

The gelatin spindle technique (Soren, 1960) involves mounting a tiny spike of gelatin—cut from a gelatin capsule—in the holder of a Straumanis X-ray powder camera. The end of the spike is moistened

so that a speck of the compound under investigation can be made to adhere to the end of the spike. Specimens weighing as little as 0.01 milligram can be photographed in 2 hours in a 57.3 mm camera. In this way, not only is positive identification made, but a permanent record is available for future reference.

The collodion film method (Gude and Hathaway, 1962) used in conjunction with a diffractometer allows rapid determination of compounds if half a milligram samples are available. The thin plastic film is stretched over the enlarged opening of a powder specimen holder, and a small amount of the material to be investigated is tapped onto the film from the straight edge of a glass slide. The plastic film eliminates background associated with a glass slide and permits resolution of faint peaks above background. Without accurate intensity data, days of calculation and manipulation would have been required to arrive at results which entailed only a few hours work using the collodion film and diffractometer.

Optical techniques were used extensively and found to be much more rapid than X-ray analysis. By the same token, however, mineral fragments which were often too fine to lend themselves to optical investigation were easily studied using diffraction techniques.

In the course of mapping the mine, some two dozen secondary minerals were collected and positively identified. Further investigation would doubtless disclose that more actually exist. For instance, one

would predict from the nature of the primary ore minerals the occurrence of secondary lead minerals in small quantities whereas none were observed. Further examination of the large fault in which the sulfates of iron and copper were noted would undoubtedly disclose additional hydrated sulfates.

The study was designed to yield information on supergene processes as they occur in an arid environment, and the species described are adequate to provide information regarding the conditions under which supergene processes work.

Previous Studies

The Pima mining district has been of great interest for some time, particularly since the recent discovery of economic mineralization. Consequently, the area has received close scrutiny both by students and professional geologists. Cooper's work (1960) gives a very general treatment of the district as a whole and presents a theory concerning the origin of the ore deposits. Lacy (1959) treats the district comprehensively and provides an alternate theory to explain the presence of mineralization.

More detailed but unpublished work on specific areas within the district has been done in the form of theses by University of Arizona graduate students. These include Mayuga (1942) whose doctoral dissertation deals with the geology and ore deposits of the Helmet Peak

area, Wilson (1960) who describes the ore controls of the San Xavier mine, Studebaker (1959) who treats the structure and stratigraphy of the Helmet Peak area, and Irvin (1959) who describes the San Xavier mine.

No previous work dealing specifically with supergene mineralogy in the district has been done.

CHEMICAL ENVIRONMENTS

Opinions vary concerning the importance of water in supergene processes. For the most part, water is considered to be the chief agent for transportation of oxygen below the surface of the earth. Lovering (1948), however, considers the "breathing" of porous rock due to fluctuation in barometric pressure to be a principal factor in the oxidation of orebodies.

The San Xavier West is a "dry" mine, i. e., nowhere does water drip from the back or walls. Timbers are generally well preserved, and dust is often a problem when working in the mine.

The temperature and the relative humidity within the workings were found to be nearly constant—the temperature at 71⁰F and the humidity at 65 percent. These measurements were made when the outside temperature was approximately 100⁰F and the relative humidity less than 10 percent.

Because of the extensive development of hydrated minerals in the apparently "dry" mine, some thought was given to the water balance of the system. A relative humidity of 65 percent at a temperature of 71⁰F corresponds to an absolute humidity of 12.6 g/m³, whereas the measurements taken outside the mine correspond to an absolute

humidity of only 4.6 g/m^3 . In spite of the absence of liquid water in the mine, water is abundant in the vapor phase. Hence, water must be present in significant quantities in the gouge-filled faults which represent the principal mode of water access and in which the most extensive supergene mineral development occurs.

With the discovery that moisture exists within the mine, it becomes meaningful to speak of the acidity, pH, of the system and of the oxidation-reduction potential, Eh, of the system.

Two distinct acidic environments are noted in the mine and are differentiated on the basis of their mineralogy. It will be shown that one environment displays minerals characteristically formed under highly acidic conditions, while the other contains minerals stable only at a much higher pH.

Control of the Chemical Environments

Faults represented the principal factor in the localization of primary ore and have since served to control oxidation by channeling supergene waters into zones of primary mineralization. Most of the underground collecting was done from faults. Variation in the nature of the faults is largely responsible for the difference in acidity and hence in the mineral assemblage related to the fault.

High pH Environment

Faults and fractures are of three principal types. Very small faults lacking gouge and primary mineralization are common throughout the mine and grade into joints. As a rule, both walls of the fracture are of the same rock type. Rainwaters moving into these small channels constitute a system originally open to CO₂ but subsequently deprived of contact with the atmosphere. Garrels (1960) has calculated the pH of such a system on theoretical bases as being 9.9 and has obtained similar values experimentally. Calcite, malachite, rosasite, hemimorphite, and aurichalcite—minerals characteristically associated with environments of low acidity—are developed and related to the fractures. Also fractures forming in fault gouge where pyrite is absent are properly included in the high pH category. Flat-lying faults, best observed on the 150-foot level, have created gouge zones composed of a fine clayey matrix with a maximum thickness of 30 feet. Talc and tremolite have been identified as important constituents of this gouge, which also contains angular fragments of carbonate rock. The clayey gouge is essentially nonreactive in the supergene environment so that minerals forming in connection with this gouge must depend entirely upon chemical content of downward-moving waters. Tabular bladed calcite, turgite, rosasite, and goethite are found in fractures within the limonite-stained gouge.

Low pH Environment

The large faults of the mine fall into two categories that constitute the second and third principal fault types. The large steeply dipping fault, which has placed the Cretaceous(?) arkose against the garnetized limestone and along which the workings trend, is the best example of an extremely acid environment. On the 150-foot level, mining has exposed this fault as well as the suite of hydrated sulfates contained within the central gouged and brecciated zone. Primary mineralization in this fault has been in the form of pyrite contained in a milky vein quartz. Recurrent movement on the fault has shattered the quartz as well as the enclosed pyrite, increasing the surface area and hence the reactivity of the pyrite.

The steeply dipping fault, which, with regard to wall-rock types, is referred to below as the arkose-garnetized lime fault, intersects the surface in a dry streambed south of the shaft leading to the San Xavier West. The fault is in a position to receive a large amount of water once or twice a year when torrential rains flood the streambed for a few days because of its location relative to the streambed. The large amount of pyrite exposed to the action of this water is responsible for the high acidity of the system. Movement of liquid water in the fault is further evidenced by the "washed" appearance of chalcantite crystals

in the fault, as if they had been partially dissolved subsequent to their formation.

Wilson (1960) shows that the steeply dipping arkose garnetized-lime fault is offset between the 150-foot level and the surface by a very flat fault. The amount of offset is small, and a zone of permeability exists in spite of this offset.

The third principal fault type is best noted on the 100-foot level where mining in a large stope has exposed the fault to view. This fault dips south at an angle of 30° and contains gouge very similar to that noted in the flat faults but in much smaller quantities. The gouge contains small well-formed crystals of pyrite, invariably coated with covellite. This pyrite, like that found on the 150-foot level, is in a state of decomposition, but the lack of water and the larger grain size have acted to retard decomposition.

A thick crust of goslarite associated with lesser amounts of chalcantite is forming directly upon the clayey gouge in this fault. Chalcocite with associated native copper and malachite are noted only beneath this sulfate crust.

The supergene mineralogy of the San Xavier West mine can best be treated by studying the two environments separately, since they are distinct in nature and mutually exclusive chemically.

PRIMARY MINERALIZATION

Basic to any treatment of supergene processes is a clear understanding of the primary minerals upon which these processes have acted.

Description of Primary Ore

Primary ore is exposed only in two places in the San Xavier West, and in both localities mineralization is fault controlled and associated with highly altered garnetized limestone. Polished sections reveal chalcopyrite, sphalerite, and galena, all of which have been emplaced in the shattered green garnet in such a way that paragenesis of the ore is quite straightforward.

The garnet, which probably approximates grossularite in composition, was highly fractured prior to the introduction of the ore minerals. The fractures have formed in such a way that the larger fissures lead into successively smaller and smaller openings, which finally terminate in unbroken garnet.

Galena was the first mineral to be emplaced in the shattered host and is found occupying even the smallest fissures adjacent to the unbroken garnet. This sulfide is not abundant, comprising perhaps 10 percent of the total ore.

Following emplacement of galena, chalcopyrite was deposited in the shattered garnet, "sealing" the galena within the garnet host. The most extensive mineralization was that of sphalerite, which exceeds both the lead and copper minerals in volume. The effect of the late emplacement of a relatively large amount of sphalerite has been to effectively "insulate" the already small amount of copper and lead within the garnet.

Oxidation of primary ore must proceed in one of two ways: either the garnet must be removed to expose the chalcopyrite and galena, or the large amount of sphalerite must be stripped away permitting oxidation of the copper and lead sulfides. In view of the nonreactivity of garnet under supergene conditions, the latter process seems most likely, and it accounts for the occurrence of the various supergene minerals along with the relative amounts of the primary minerals.

The paucity of pyrite is an important feature of the primary ore. In all the polished sections made of primary ore, only one fragment was noted in a single section. This fragment was badly corroded and in a state of extensive decomposition resulting from supergene oxidation.

Pyrite is common only in the shattered milky quartz of the arkose-garnetized lime fault. The quartz, as well as the enclosed pyrite, has been badly shattered, and pyrite is decomposing rapidly due to the volume of water moving in the fault.

Tiny cubes of pyrite are noted in the clayey gouge of the 100-foot level stope. These cubes are not broken as are those from the level below, but unlike the pyrite found in the milky quartz, these small crystals are coated by a thin film of iridescent covellite.

Clearly, some acid has been available from the decomposition of pyrite, but just as clearly this has been of limited amount, which may account for the lack of enrichment.

Temperature of Primary Mineralization

An effort was made to determine the temperature of primary mineralization. The most convenient method was the sphalerite geothermometer. The unit cell constant of sphalerite was carefully measured using X-ray diffraction techniques. Values of a_0 were extrapolated to $\sin^2 \theta = 1$, and a best value of 4.4180 \AA was obtained.

Unit cell size was then related to mole percent FeS by the method of Skinner, Barton, and Kullerud (1959).

$$a_0 + 5.0493 = 4.56 \times 10^{-4} \text{ (mole percent FeS)}$$

$$\text{mole percent FeS} = \frac{5.4180 + 5.0493}{4.56 \times 10^{-4}} = 19.1 \text{ percent}$$

Iron saturation cannot be proven despite the large quantity of FeS present in the sphalerite so that the temperature of approximately 500°C that corresponds to 19.1 mole percent FeS is a minimum.

While only a minimum value of temperature is available, this is the minimum temperature for the most extensive phase of mineralization and is helpful in that respect. The object was to determine an approximate temperature of formation for the sphalerite, and, because of the time and effort involved in such an analysis, only one sample was measured. The quality of this measurement is, however, rather good as shown by the linearity of the points on the a_0 versus $\sin^2 \theta$ plot (fig. 1).

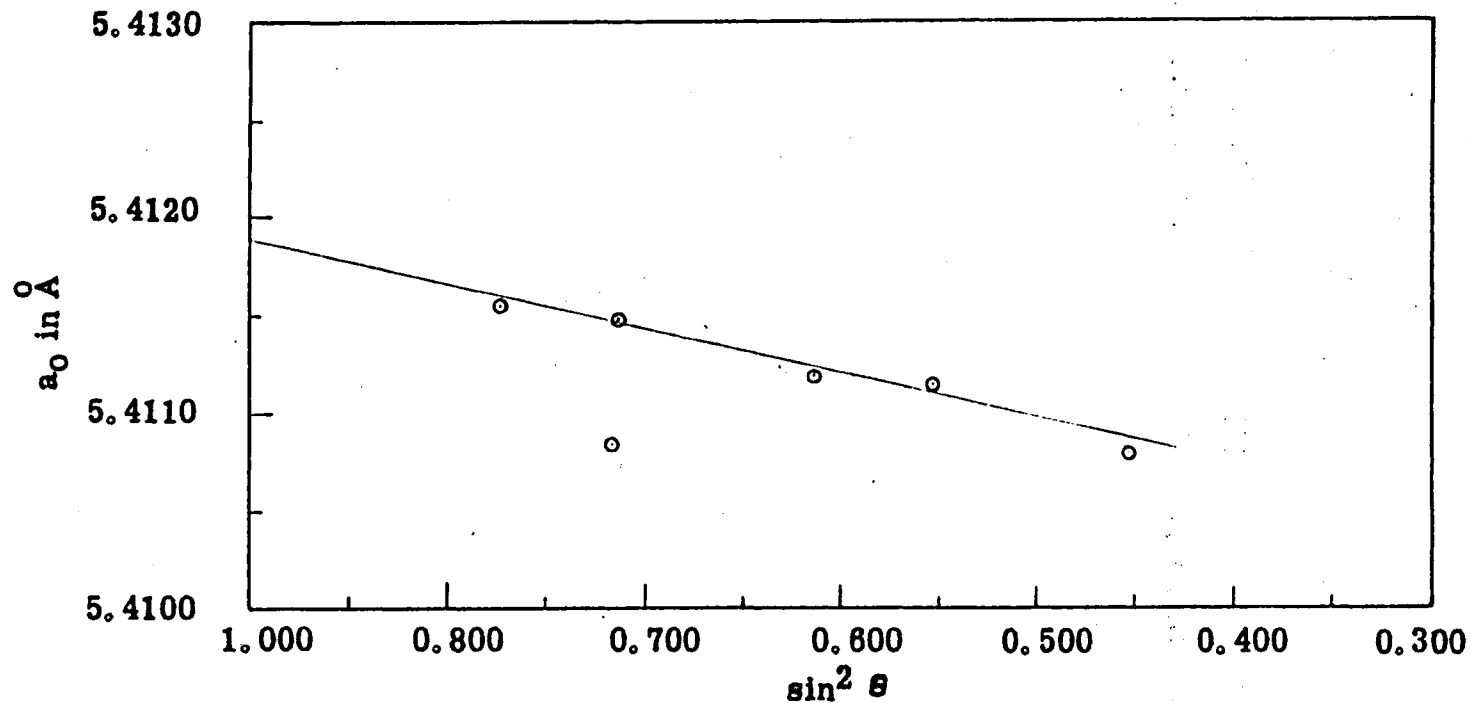


Figure 1. -- Plot showing extrapolation of a_0 values calculated from three high θ lines to $\sin^2 \theta$ equal 1. Best value of a_0 is obtained as 5.4180 angstroms.

SUPERGENE SPECIES AND THEIR OCCURRENCES

Aragonite, CaCO₃

Only one occurrence of aragonite was noted within the mine. The mineral occurs on a fragment of rock which had fallen from the back. The efflorescence is about 2-1/2 inches in diameter and consists of a great number of small but perfectly formed acicular crystals, apparently unrelated to cracks or fissures.

Aurichalcite, 2(Zn, Cu)CO₃ 3(Zn, Cu) (OH)₂

Aurichalcite was noted only rarely in the large stope on the 100-foot level. The mineral is blue white in color, having an excellent micaceous cleavage and occurring as flakes upon the clayey gouge. These flakes seem unrelated to cracks or fissures or to other minerals and occur randomly in the stope, commonly in very small groups 1/4 to 1/2 centimeter in diameter.

The lack of chemical stability and free energy data on aurichalcite limits its use as an indicator of environment, but similarity to rosasite and malachite may extend to conditions of equilibrium. In any case, aurichalcite is hardly an unexpected mineral in the oxidized zone of a copper-zinc deposit.

Brochantite, $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$

Brochantite was found in the large arkose-garnetized lime fault on the 150-foot level and sparingly in the 100-foot level stope. Identification of the basic sulfate was confirmed by X-ray diffraction. The mineral occurs as a light- to dark-green powder within fractures in, and as crust upon, milky quartz or garnetized limestone (fig. 2). The darkness of color depends upon the amount of intermixed covellite, the occurrence and relationship of which will be discussed below.

Jarell (1944) in his work at Chuquicamata finds that sulfates in general are formed by precipitation from solution and not as replacement of original sulfides and that brochantite in particular forms from solutions having a low concentration of SO_3 , while chalcantite results from solution of high concentration of SO_3 . Garrels (see Anderson, 1955, p. 332), on the other hand, emphasizes the importance of pH in the formation of supergene sulfates, claiming that brochantite results from neutralization of dilute cupric sulfate solutions, while chalcantite forms by evaporation of solutions having high cupric sulfate concentration.

In the San Xavier West mine, brochantite has clearly formed from solution, and a possible process will be discussed in a later section.

FIGURE 2

**Brochantite (light green), melanterite, and
chalcanthite upon shattered milky quartz. Note
powdery nature of brochantite.**



Calcite, CaCO₃

Calcite is present throughout the mine where the high pH environment prevails. Calcite is most commonly noted as thin crusts or small fissure fillings, but at two locations the occurrence is particularly noteworthy.

In the large stope on the 100-foot level, calcite has formed in openings resulting from fracturing of the clayey gouge and is associated with turgite, goethite, and rosasite. The calcite crystals are tabular, extremely flattened rhombs, which vary in size from barely visible to 5 mm.

The quality of the crystal faces prevented exact goniometric work, but approximate measurements indicate that the forms involved are probably $\{03\bar{3}2\}$ or $\{05\bar{5}4\}$ in conjunction with $\{0001\}$.

On the 100-foot level in a large open fissure, perfect acute scalenohedrons and rhombohedrons were observed forming a coarse drusy over limonite, not unlike the occurrence of quartz noted below. These crystals, although exceedingly small, are of the optical variety of calcite.

Chalcanthite, CuSO₄ · 5H₂O

Chalcanthite forms as a product of the decomposition of pyrite in the arkose-garnetized lime fault on the 150-foot level. The

bright-blue sulfate coats the general vicinity of the fault but is most abundant in the central gouged and brecciated areas. Crystals range in size from barely visible to 5 mm in length, but no well-formed crystals were found. All were badly rounded as if they had been partially dissolved by waters moving downward in the fault zone.

The steep fault in which the chalcantite is noted intersects the surface in a streambed, and, while this fault is somewhat offset by the large flat faults that transect it, a zone of permeability could still exist and provide a channelway for waters to move downward.

Chalcantite is metastable under the ambient conditions of the laboratory (circa 76°F and 51 percent relative humidity), but only partial decomposition to $\text{CuSO}_4 \cdot ?\text{H}_2\text{O}$ was noted in the course of several months.

The association of chalcantite with brochantite (see above) is anomalous, and their exact process of formation deserves mention. The precipitation of chalcantite is such a rapid process that paragenesis is of almost no help since several generations of the sulfate could easily be observed in the same hand specimen.

Chalcocite, Cu_2S

The chalcocite is found only with malachite in the 100-foot level stope. The sulfide, although most likely secondary, is of the steely variety and does not soil the fingers. The chalcocite occurs in

finger-size fragments beneath a crust of goslarite. These fragments of chalcocite are covered with excellent crystals of malachite and gypsum, the latter containing bright native copper. Polished sections reveal that malachite is replacing chalcocite (fig. 3).

While chalcocite is not abundant, its presence strongly suggests that some enrichment has taken place, assuming that the chalcocite found is secondary. The term enrichment is used in the sense of replacement governed by Schurrmann's series (Garrels, 1954) and occurring below the stability boundary shown in figure 4. Enrichment, therefore, need carry no connotation of the formation of a sizable blanket of secondary sulfides but implies only a set of conditions suggested by the stability curve. Replacement by chalcocite was extensive, and no evidence remains of the material at whose expense chalcocite was formed.

Chrysocolla, $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$

Chrysocolla is found throughout the mine, both underground and on the surface. It does not occur when pH is extremely low and is generally associated with the dark oxides of iron or manganese. When found with malachite, the malachite has invariably formed later than the chrysocolla.

FIGURE 3

Steely chalcocite barely visible beneath replacing malachite. Specimen approximately 2 inches x 3/4 inch.



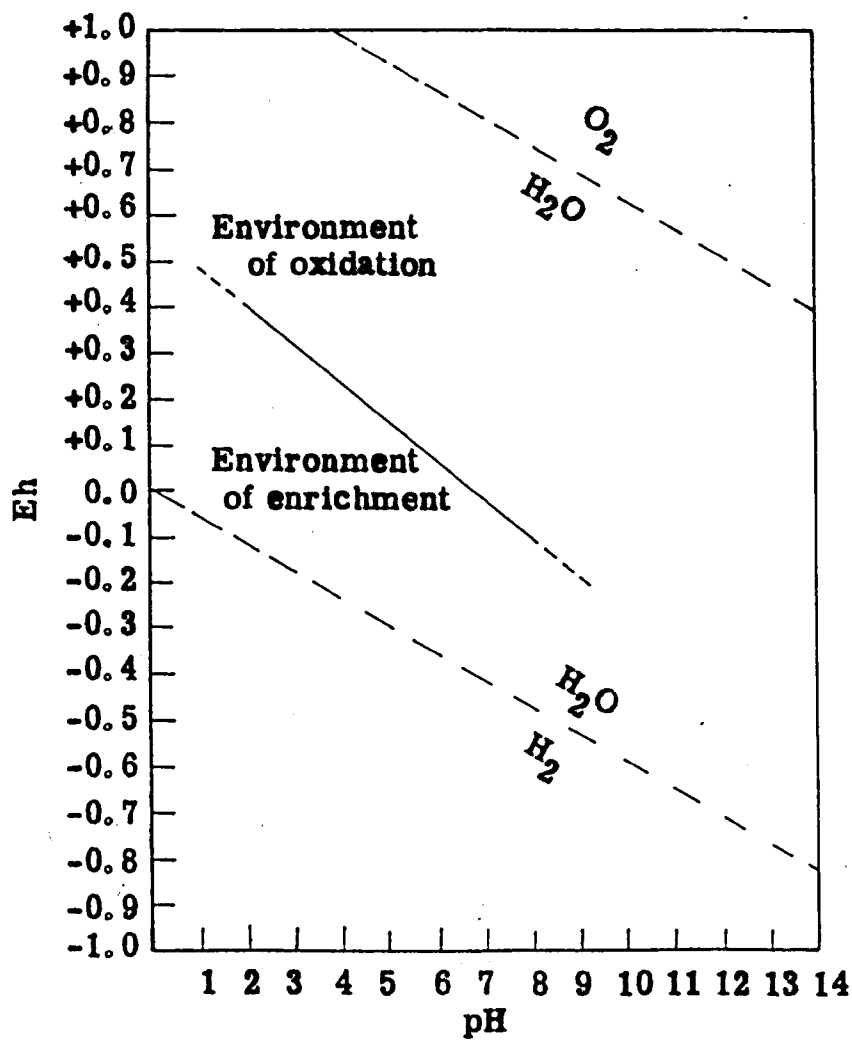


Figure 4. --Environments of oxidation and enrichment defined on the basis of mineral stability. Modified from Garrels (1954).

Native Copper, Cu

Native copper was found only in the 100-foot level stope associated with chalcocite and malachite and completely encased in gypsum (fig. 5). The tiny fragments (no crystals were observed) exhibit a hackly surface and have a bright untarnished metallic luster. In places where a portion of the fragment extends beyond the protective covering of gypsum, the copper has been converted to malachite.

The discovery of the untarnished native copper associated with malachite and chalcocite serves quite nicely to trace the history of the zone of enrichment from the time when conditions were suitable for the formation of chalcocite through a steady rise in oxidation potential to the present highly oxidizing environment in which malachite is forming to replace the chalcocite. This change in environment will be treated in some detail in a later section.

Coquimbite, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

Coquimbite has been identified occurring as a thin crust on the walls of the workings near the arkose-garnetized lime fault on the 150-foot level where it is associated with chalcocite and melanterite. The mineral occurs as minute sulfur-yellow crystals that smear rather than powder upon grinding.

FIGURE 5

Tiny fragments of native copper within a striated gypsum crystal. Note untarnished surface of enclosed copper fragments. Gypsum crystal approximately 2 mm x 1 mm.



Identification of the mineral is based upon its association and the description (Palache, Berman, and Frondel, 1952) of coquimbite. Also a diffractometer tracing made from coquimbite taken from the University of Arizona Mineralogical Museum matched that of the coquimbite from the San Xavier extension.

Measurement of the average index of refraction was necessitated by the small size of crystals. This index was found to be 1.548 as compared to the published value of 1.554 for coquimbite from Arizona (Palache, Berman, and Frondel, 1952).

Particular care was taken with the identification of coquimbite because of its usual occurrence as a mine-fire mineral. In the stope where the coquimbite was found, several badly charred round timbers were noted, indicating the possibility of a sizable fire in the stope at one time. The coquimbite was found directly over an ore chute leading down to the sublevel between the 150-foot level and the 270-foot level. A draft moving through the ore chute would have drawn smoke downward past the small section of the wall on which the coquimbite was found. This area of the wall is the scene of a large concentration of melanterite, chalcantite, and brochantite. Since coquimbite is not found in other parts of the stope, it may be formed by the alteration of one or more of the hydrated sulfates. However, the area in which coquimbite is found received a large volume of supergene water, and unless the rather tenuous relationship between mine fires and coquimbite is clarified, its

formation is more logically attributed to the same waters that precipitated the chalcantite and melanterite. In further support of the latter idea, no instance of replacement of any sulfate by coquimbite was noted.

Covellite, CuS

The occurrence of covellite is limited to the low pH environment where it occurs as an iridescent coating upon decomposing pyrite or as a thin film over brochantite. The occurrence on pyrite is quite straightforward, but the association with brochantite is slightly unusual and, for this reason, merits some attention.

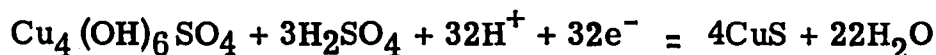
Covellite was first noted within a small fissure in shattered milky quartz and when scratched appeared to yield a green streak. Closer examination revealed that the covellite was merely a film and that the green streak resulted from the underlying brochantite. Final proof that the mineral was covellite was obtained using the collodion film technique mentioned above and eliminating brochantite peaks on the diffractometer tracing.

No transition phase was noted between the covellite and brochantite, although one could have been overlooked because the amount of covellite was quite small and the film quite thin.

Bateman (1950) notes that covellite tends to precipitate where the ratio of ferric to ferrous iron is high and chalcocite where the reverse is true. However, Garrels' (1960) later work showing that the

activity of ferric iron is negligible at pH greater than 2 casts some doubt upon this former theory.

A possible reaction to form covellite from brochantite in the presence of H_2SO_4 might be as follows:



in which

$$\Delta F_R^0 = -327.34 \text{ kcal/mole.}$$

The reaction would be a surficial reaction only because, once a film of covellite is formed, the brochantite would be effectively removed from reaction by the film of covellite which is stable even at very low pH, and which would resist the action of sulfuric acid preventing its contact with brochantite.

This process accounts for the relative amounts of the minerals observed and for the occurrence of covellite only as a film without a transitional phase. The intermixing of brochantite and covellite can be explained either by some mechanical disturbance along the fault or by repeated formation of brochantite and covellite, perhaps in some sort of seasonal cycle dependent upon the availability of water solutions to deposit brochantite.

Goethite, FeO(OH)

Goethite is found with calcite, rosasite, and turgite growing in fissures formed in the clayey gouge of the 100-foot level stope (fig. 6).

FIGURE 6

A fragment of clayey gouge. Forming in the fissures are tabular crystals of calcite as well as turgite, goethite, and rosasite. Specimen approximately 5 inches x 3 inches.



Crystals of goethite that pierce the flat-bladed calcite are dark brown in reflected light but blood red in transmitted light and have assumed a "shell-like" form as if they had formed as a coating after which the host material had been removed. The shape of the shells suggests that the host may have had the crystal form of an elongate prism similar but slightly larger than the prisms of quartz found in other parts of the mine.

No good free energy data are available for goethite, but its similarity to hematite permits hematite data to be substituted (Garrels, 1960).

Goslarite, $ZnSO_4 \cdot 7H_2O$

Goslarite is the most abundant single supergene mineral found in the San Xavier West mine. It is found in almost every area having slight to moderate acidity and in some faults is so prominent as to form a thick crust.

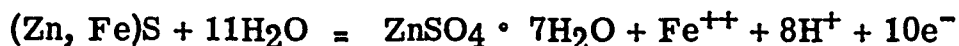
Crystals of goslarite are very slender elongate forms invariably singly terminated. One crystal found in the 100-foot level stope was about as thick as a human hair and measured over 7 inches in length. Some variation in color is noted, namely the acquisition of a light-blue shade (cuprogoslarite) reflecting the absorption of copper.

Careful X-ray measurements indicate that this particular sulfate is neither the hexahydrate nor the heptahydrate but apparently lies somewhere between the two forms. This phenomenon is common in hydrated sulfates, the intermediate hydration state probably resulting from loss of water due to dehydration upon removal from the mine.

Because goslarite is usually a very late mineral in the paragenetic sequence, the existence of some intermediate form between sphalerite and goslarite was expected, but none was noted. Goslarite appears to form directly upon the clayey gouge or limestone wall rock and is not an alteration product (fig. 7).

Possible processes for the decomposition of zinc through various intermediates to yield goslarite were considered. Most reactions investigated that involved transitional phases proceeded against a slight energy gradient. Also, attempts to locate some intermediate zinc compound were in vain. A possible mechanism for the decomposition of sphalerite and formation of goslarite is shown below.

Recalling from the geothermometry work with sphalerite that it contains approximately 19 mole percent FeS, we may write:



where (Zn, Fe) is assumed to have a value of F^0 about the same as ZnS above. (If anything, the true value would be slightly greater.) $\Delta F_R^0 = +38.79$ Kcal/mole for the above reaction.

FIGURE 7

Crystals of goslarite, on this specimen almost completely dehydrated, have formed directly upon the clayey gouge of the 100-foot level stope. Width of field approximately half an inch.



$$Eh = E^0 + \frac{0.059}{10} \log \frac{[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}] [\text{H}^+]^8 [\text{Fe}^{++}]}{[(\text{Zn, Fe})\text{S}] [\text{H}_2\text{O}]}$$

in which all activities are assumed to equal unity except that for Fe^{++} which is taken 10^{-6} and $[\text{H}^+]$ which is variable.

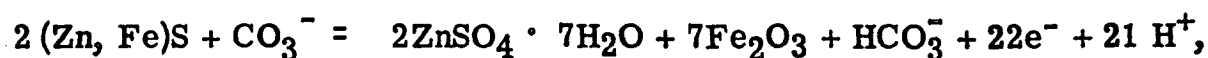
$$E^0 = \frac{38.79}{(10)(23.06)} = +0.1618 \text{ volts.}$$

$$Eh = +0.1681 + 0.0059 - 6 - 0.0059 (8 \text{ pH})$$

$$Eh = 0.1327 - 0.0472 \text{ pH}$$

The plot of this stability curve is shown in figure 8. The curve as determined lies nearly parallel to the boundary between sphalerite and goslarite as determined by Kothavala (Schmidt, 1962, p. 157) but approximately 0.2 volts below Kothavala's line.

Having established that goslarite is the stable phase under nearly all oxidizing conditions there still remains the problem of the energy gradient which, as shown above, is +38.79 Kcal/mole. If the reaction is written



which is probably a more realistic approach, the reaction may proceed with a free energy decrease of -893.19 Kcal/mole. The stability region of the products is seen on inspection (because of the complex nature of the reaction involving bicarbonate and carbonate species, detailed calculation would be impossible without some rather unwarranted assumptions) to encompass the stability field of water under normal conditions.

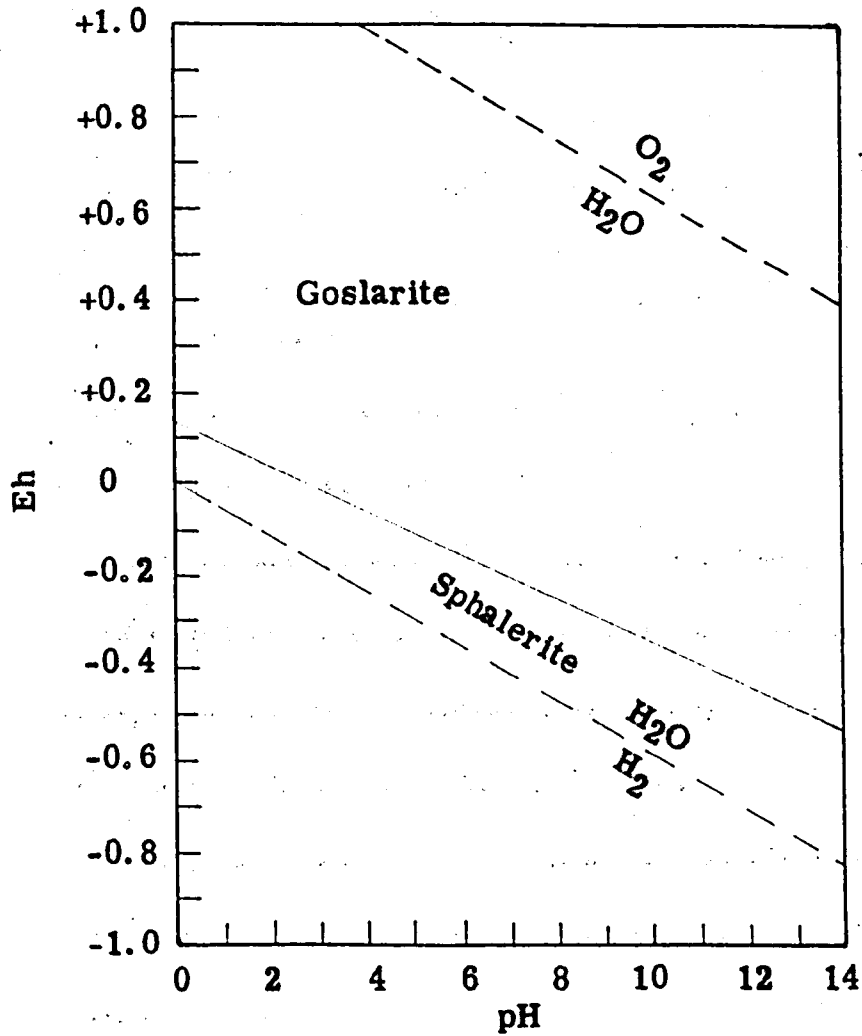


Figure 8. --Stability relations between goslarite and iron-bearing sphalerite at 25°C, and 1 atmosphere total pressure in the presence of water. Fe^{++} taken as 10^{-6} .

Thus, even slight involvement of the ferric ion and/or the bicarbonate ion could lower the ΔF_R^0 value significantly and remove the slight energy gradient noted for the decomposition of zinc to form goslarite.

Although we have demonstrated that the occurrence of zinc in the form of goslarite is normal, formation of the mineral in the mine is not yet explained. The lack of a transition stage and the character of the crystals lead to the nearly inevitable conclusion that goslarite, in which form most of the zinc is found, has been formed upon the clayey gouge from solution.

Clearly, most of the goslarite observed has formed subsequent to mining operations.

Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Gypsum is found only in small quantities associated with chalcocite, malachite, and native copper. This sulfate occurs in well-formed striated crystals exhibiting a prominent $\{010\}$ cleavage.

Gypsum is later than chalcocite because it often contains impurities of that mineral and earlier than malachite, which often forms over the gypsum. The contemporaneity of native copper and gypsum is critical, and it is firmly established by the occurrence of the former mineral suspended within the crystals of gypsum.

Hematite, Fe₂O₃

Hematite is notable in the San Xavier West mine if for no other reason than its remarkable abundance. Two varieties are present: red powdery hematite and steely specularite. The latter variety grades into turgite having a low iridescence.

Hematite of the powdery variety occurs in the large south-dipping faults where garnetized limestone is present. Because these faults have served as channelways for "ore-bearing fluids," the margins have suffered extensive alteration to a green garnet, which is probably grossularite. Mining has followed these faults and provides excellent exposures of the alteration zone. Any slight movement along the hematite-laden fault tends to smear the hematite and to impart a sanguine aspect to the fault zone.

Specular hematite appears in surface pits north of the No. 6 shaft where the above-mentioned faults and their alteration zones have been penetrated. Specularite forms in circular groups of closely spaced radiating crystals whose metallic luster varies from bright to dull, probably depending upon the extent of weathering. These groups may attain a diameter of 5 mm and are generally formed upon silicated limestone.

A thorough treatment of the origin and occurrence of hematite is beyond the scope of this paper. Thin sections do reveal, however,

that while some hematite is primary and of approximately the same age as the zoned green garnet, a large portion is apparently surficial. This hematite is noted in large quantities in hand specimen but does not survive grinding and washing so as to appear in thin section. A study of alteration, which would include an investigation of hematite, would be particularly interesting in light of the small amount of pyrite associated with the primary ore.

The status of turgite as a mineral species is doubtful (Ford, 1932), and for this reason it will be included as a variety of hematite.

The iridescent oxide appears with calcite and rosasite in areas of high pH. Turgite is much less abundant than hematite and limonite, but several very nice botryoidal specimens were collected. The iridescence of turgite varies greatly even within a single hand specimen. A sample of turgite several millimeters long is often highly iridescent on one end and noniridescent on the other, where it assumes a steely luster not unlike specularite. No attempt was made to determine whether turgite actually graded into specularite.

Hemimorphite, $H_2Zn_2SiO_5$

Two distinct varieties of the zinc silicate are noted in and about the mine. Hemimorphite occurs on the surface as crystals of small size and poor quality or as nodular masses within the spongy

network of a gossan. The former variety resembles hemimorphite in every way, but the nodules have a hardness of 6 to 7 on the Mohs scale. Because of this anomaly in physical properties, the presence of willemite was at first suspected, but X-ray analysis and optical work confirmed that both varieties are hemimorphite. The difference in physical properties is presumably due to weathering, the harder nodular variety being found in an unprotected situation while the crystals were partially shielded.

Inside the mine hemimorphite occurs in excellent crystal forms (fig. 9). Many of the tiny crystals (the largest crystals found were 4 mm in length) are doubly terminated and exhibit the hemimorphism of the $mm2$ class admirably. The crystals are found in thumbnail-size aggregates associated with tiny fissures and vugs of the limestone wall rock and clayey breccia. Chemical data concerning hemimorphite are lacking, but it clearly forms under neutral to slightly alkaline conditions.

Limonite, Approximately $2Fe_2O_3 \cdot 3H_2O$

The name limonite is applied to hydrated iron oxides of ubiquitous occurrence within the mine. Varieties extend from the brownish-yellow stain, coating nearly all of the clayey gouge in the 100-foot level stope, to the shiny black botryoidal material, which occurs with the

FIGURE 9

A cluster of hemimorphite crystals. Length of crystals approximately 2 mm.

hydrated solution as the large influence of the
change of the molecular arrangement on the
macroscopic behavior.

The whole system is in a state of
equilibrium between the solid and the
liquid or gaseous phase. The whole system
is in a state of equilibrium between the
solid and the liquid or gaseous phase.



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Mineralogy, Vol. 1, p. 100

The whole system is in a state of
equilibrium between the solid and the
liquid or gaseous phase. The whole system
is in a state of equilibrium between the
solid and the liquid or gaseous phase.

hydrated sulfates in the large arkose-garnetized lime fault. The abundance of the material eliminates any usefulness it may have had as an environmental indicator.

One notable qualitative observation was made, however, concerning the nature of limonite. The oxide generally occurs as a tan stain or yellow-brown powder in an environment of high pH, but when the pH is low the limonite is formed in shiny black botryoidal masses.

Malachite, $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2$

Malachite is observed in most parts of the mine where pH is fairly high and on the surface as a stain in and near faults. Good crystals of malachite, however, are found only with chalcocite in the 100-foot level stope. These crystals are emerald green and occur in radial aggregates. Individual crystals may reach a length of 1 mm, and polished sections of chalcocite reveal that malachite is replacing the sulfide. When malachite occurs with chrysocolla, it forms very poor crystals and is, for the most part, massive.

Melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Melanterite is similar in occurrence to chalcantite with which it is nearly always associated. Like its copper counterpart, chalcantite, this green sulfate occurs abundantly, but crystals are the rounded

washed forms similar to those of chalcantite with the rounding presumably resulting from the same cause.

In spite of its intimate association with chalcantite, melanterite is always sharply delineated from chalcantite, which serves to underscore the marked structural difference stemming from the presence of two essential water molecules. Even though chalcantite and melanterite are members of solid solution series (Palache, Berman, and Frondel, 1952), the two species are not mixed. Unlike chalcantite, melanterite does not decompose under the prevailing laboratory conditions, viz. 71°F and 51 percent relative humidity (fig. 10).

Quartz, SiO₂

In addition to the quartz that occurs in the arkose, two distinct occurrences are noted in the mine. Along the fault contact between the Cretaceous(?) arkose and the garnetized limestone, slightly milky highly shattered massive vein quartz is noted. Pyrite cubes within the quartz are also shattered, probably from recurrent movement on the fault.

Secondary quartz crystals are noted in areas of high pH where percolating waters have deposited the crystals in fissures and vugs. The crystals are clear hexagonal prisms, singly terminated by first

FIGURE 10

Melanterite (green) and chalcantite (blue) on a fragment of shattered milky quartz from the arkose-garnetized lime fault. Note partial dehydration of chalcantite to $\text{CuSO}_4 \cdot ?\text{H}_2\text{O}$ (white). Specimen is approximately 4 inches by 2 inches.



order bipyramids, which vary in length from a few millimeters to 1-1/2 cm.

Near the shaft in a limestone fissure on the 100-foot level, thin spherical shells of quartz are noted covering a brown material. This material was never conclusively identified but is apparently of a clayey nature. The quartz shells have a drusy outer surface and decidedly metallic luster when viewed in strong light. The shells of quartz are all similar in size and shape and are approximately 5 mm in diameter.

Rosasite, $(\text{Cu, Zn})_2(\text{OH})_2\text{CO}_3$

Rosasite is noted only in the 100-foot level stope. The crystals are a very light shade of blue and of such small size that the spherical aggregates, which they form, have a "fuzzy" aspect. The individual crystals are invisible to the naked eye, but the aggregates of such tiny crystals often attain a diameter of 3 mm. The interior of these spherical aggregates is a much more compact form of rosasite, suggesting the possibility of a compositional change toward the center of the spheres; however, no such differences could be detected between the compact and soft varieties.

Rosasite is found intergrown with the flat-bladed variety of calcite. It is also found on freshly fractured surfaces, suggesting that it may have formed subsequent to mining operations.

Smithsonite, ZnCO₃

Smithsonite was sought diligently with the thought that it might be a transitional stage between sphalerite and goslarite. The only specimen of this carbonate collected consisted of a thin crust on a small splinter of wall rock from the 100-foot level stope.

Unidentified Compound, ?

This material was found on the 100-foot level near the main shaft. It was located in a limestone fissure and was entirely covered by a spherical shell of drusy quartz. The compound is a greasy coarse powder having a dark seal-brown color but lacking crystal form.

The powder was X-rayed and found to be amorphous, a result anticipated from preliminary microscopic investigation. It was then subjected to spectrographic analysis with the following result:

Element	Visual Estimation of Line Intensity
Mn	Strong
Ca	Strong
Zn	Strong
Cu	Strong
Mg	Strong
Si	Strong

The presence of such a large number of cations, all of which are present in significant quantities, leads to the conclusion that the powder is probably not a supergene mineral at all but some sort of hydrated clay in which several phases are present or which has a poorly developed crystal structure. Such a clay could easily absorb various cations from waters in amounts sufficient to be observed spectrographically. Why the "clay" formed in spherical aggregates to be coated by a thin spherical shell of drusy quartz is not known.

Varicolored materials of clayey character were commonly observed but are not well understood. The colors that can be assumed by such material as this are of great variety and apparently depend upon the nature and amount of various cations. Often several days were spent working on a "mineral" only to learn that it was another variation of the "clay theme."

THE USE OF ENVIRONMENTAL INDICATORS

Once the major mineral species in the San Xavier West mine were determined and some ideas concerning their genesis formulated, an attempt was made to combine the stability relations of several related species in an effort to arrive at some conclusions regarding the nature of the supergene environment.

The first relationships to be studied were those existing in the highly acidic zone of the arkose-garnetized line fault. Minerals present in this fault include pyrite, melanterite, chalcantite, and brochantite. Stability diagrams from these minerals were excerpted from published diagrams (Schmidt, 1962) and are shown below. With the total dissolved sulfide concentration of 10^{-1} , chalcantite has a wide stability field whose Eh is limited only by the stability of water, and brochantite has a similar but slightly narrower range of stability (fig. 11). The melanterite field is confined by hematite to Eh values of less than about +0.7 and to pH values of less than 4.0 (fig. 12). Superposition of the melanterite field upon the chalcantite field (fig. 13) shows that the area common to both minerals lies within an Eh range of +0.3 and +0.7 and between a pH of 0 and 3.

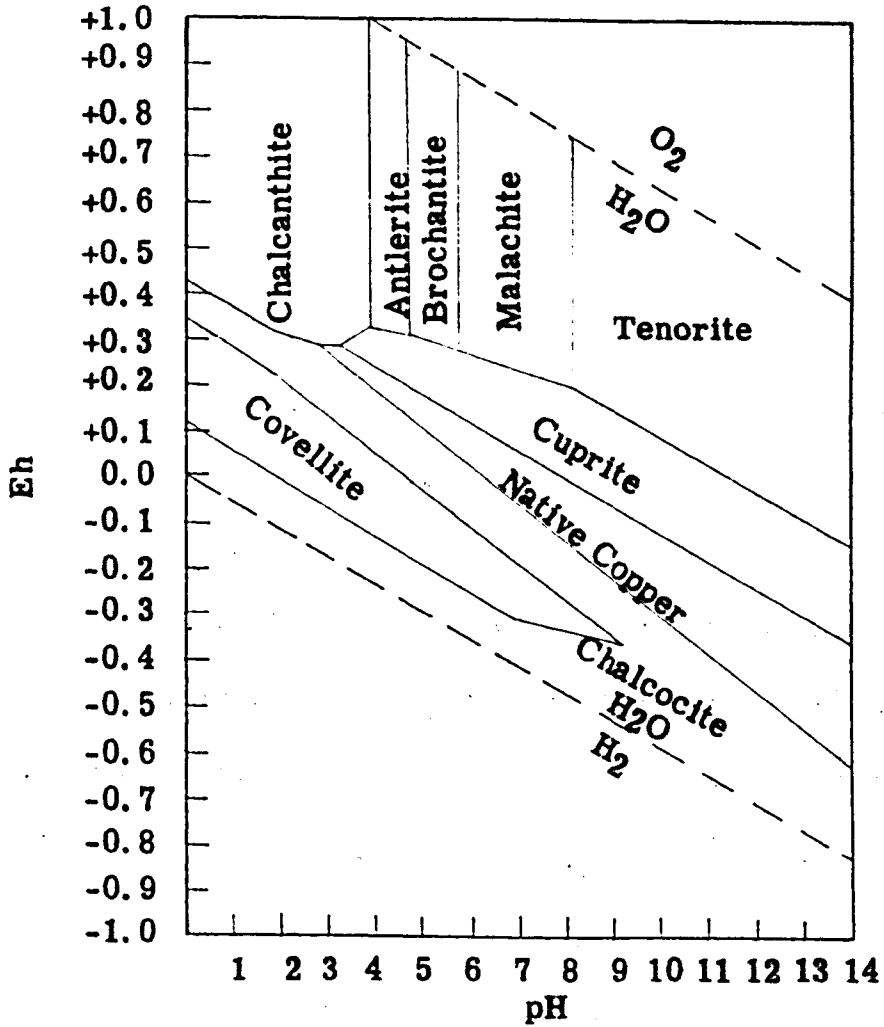


Figure 11. --The system Cu-S-C at 25°C, and 1 atmosphere total pressure in the presence of water. Other conditions: Total S = 10^{-1} ; total CO₃ = 10^{-3} . From Schmidt (1962).

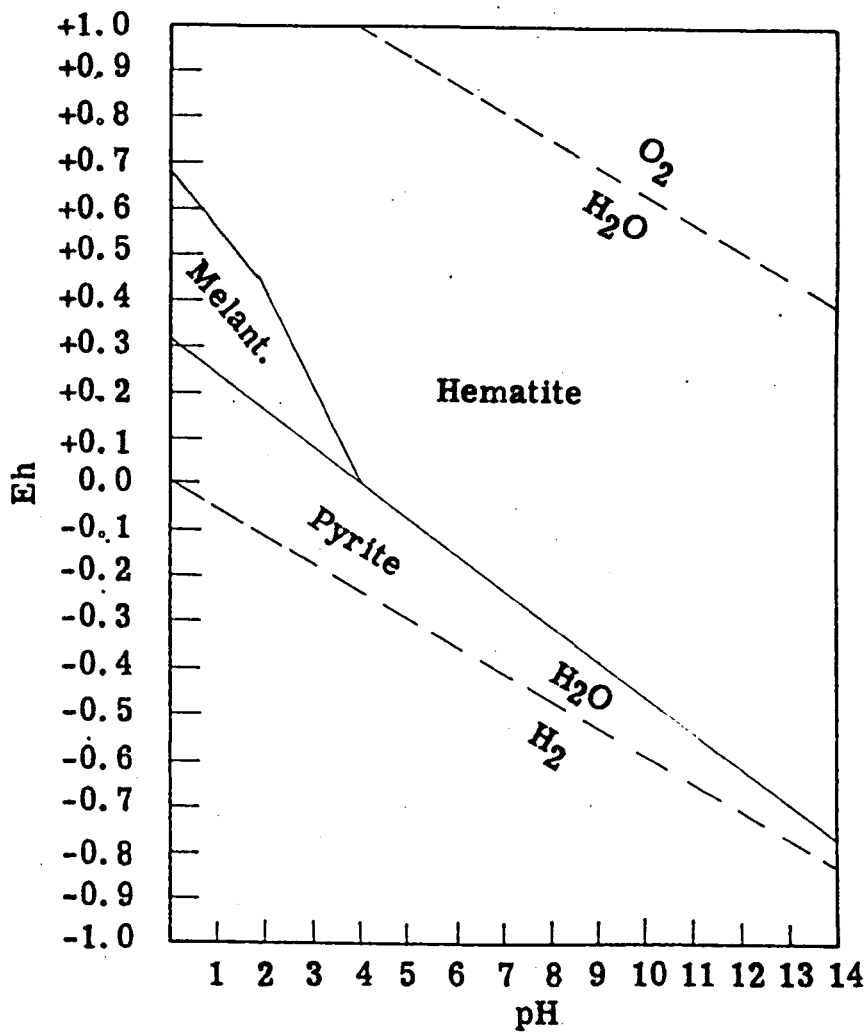


Figure 12. --Stability relations of some iron minerals at 25°C, and 1 atmosphere total pressure in the presence of water. Total S = 10⁻¹: Modified from Schmidt (1962).

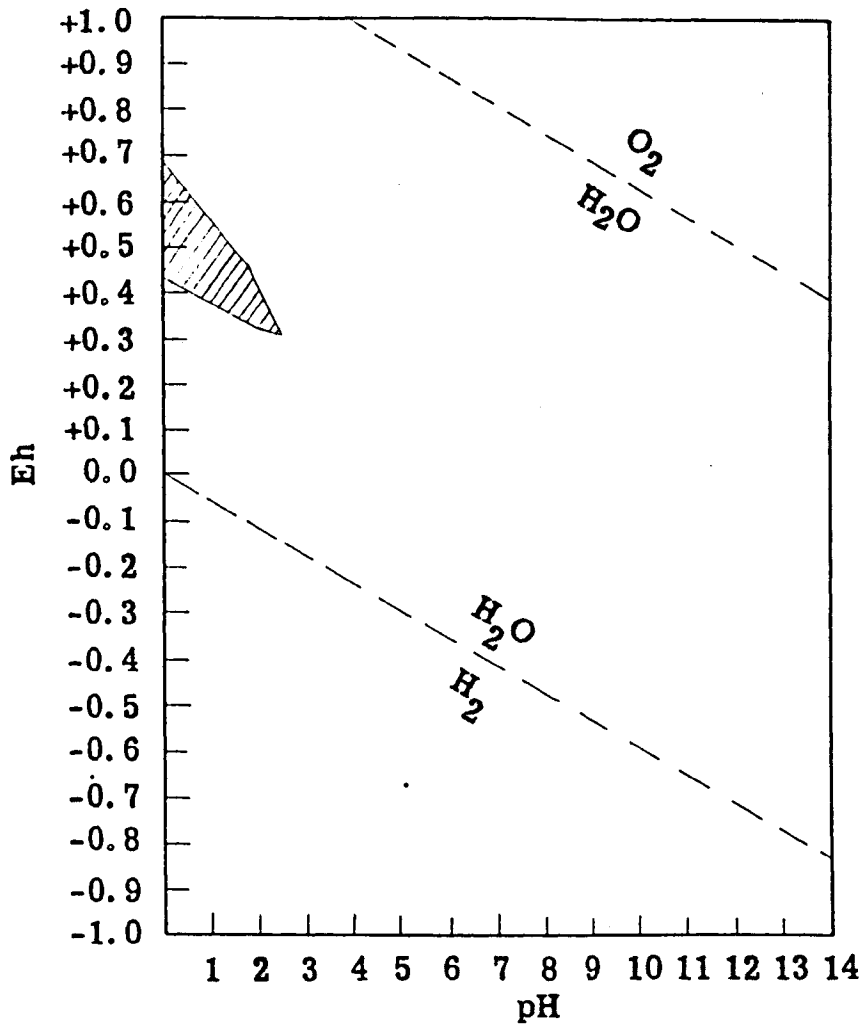


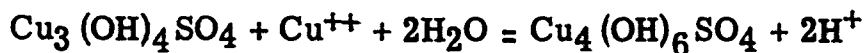
Figure 13. --Mutual stability field of chalcantite and melanterite at 25°C, 1 atmosphere total pressure in the presence of water. Total S = 10⁻¹.

The extreme acidity of the zone appears to be the result of oxidation of pyrite in relatively nonreactive surroundings, i. e., in an environment of low carbonate concentration.

Brochantite has a field of stability in the pH range from 4.8 to 5.8, and Eh may vary from +0.3 upward to the stability of water in this pH range. In view of the close association of chalcantite and melanterite with brochantite, the assumption of similar upper Eh boundaries for the system, which includes brochantite, seems reasonable.

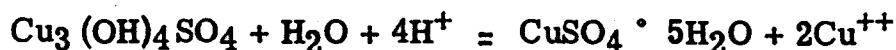
Assuming similar values of Eh for the environment, the problem of antlerite, whose stability field should lie between that of chalcantite and brochantite, still exists. Drawing conclusions from the absence of a mineral species is obviously dangerous, but the absence or at least the paucity of various species is theoretically interesting.

A reaction to form brochantite from antlerite can be written:



$$\Delta F_R^0 = -67.055 \text{ Kcal/mole,}$$

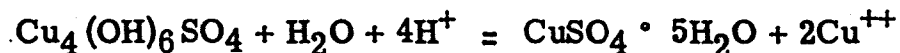
and to form chalcantite from antlerite,



$$\Delta F_R^0 = -16.05 \text{ Kcal/mole.}$$

From the above antlerite appears to be metastable with respect to chalcantite, and if formed, would tend to give way to brochantite or less readily to chalcantite.

A logical question now concerns the appearance of both chalcantite and brochantite when the reaction



$$\Delta F_R^0 = -24.78$$

predicts that brochantite should have a tendency to form chalcantite. The intimate association of chalcantite and brochantite seems distinctly anomalous if one recalls Garrels' suggestion, cited above, that chalcantite may form from evaporation of concentrated cupric sulfate solutions having low pH, antlerite from neutralization of such solutions, and brochantite from the neutralization of very dilute solutions.

Consideration of the unique environment may provide at least a partial answer. If the fault leading to the streambed on the surface were suddenly flooded, as by a torrential rain, the first solutions moving through the fault might reach the 150-foot level in a matter of hours, while the last waters trickling into the fault might require several weeks to penetrate to this depth. The last waters to reach the second level of the mine, having soaked for some time in the pyrite-laden fault, would have a pH much lower and a sulfate concentration much greater than the earlier waters that spent only a few hours in the fault.

This could account for the formation of both minerals in the same place. Still, the problem of alteration of brochantite to chalcantite remains. Rather than try to circumvent this process, I believe that it

is actually occurring and cite the crumbly noncrystalline nature of the brochantite and the well-formed (if slightly "washed") appearance of the chalcantite crystals as evidence.

In the final analysis, considering the field of stability of melanterite and chalcantite and the metastability of brochantite, the pH must lie between 2 and 3 at an Eh of +0.3 to +0.6.

The conditions prevailing in the 100-foot level fault are less easily predicted than those in the arkose-garnetized lime fault, but they provide a history of the ore deposit and its oxidation not found in the latter fault.

The presence of small fragments of pure chalcocite implies that enrichment has taken place, but it provides no real information on the nature of the attacking solutions or the mineral(s) at whose expense chalcocite was formed. The discovery of fragments of chalcocite and native copper suspended within crystals of gypsum indicates that, subsequent to enrichment, the Eh was increased, and probably the pH was reduced to form native copper that has been preserved in the gypsum. Doubtless gypsum was deposited from the very solutions which tended to change the environment, but even establishment of this close relationship does not provide information concerning the nature of the solutions themselves because of the very large stability range of gypsum.

Following the partial oxidation of chalcocite to form native copper, malachite formed. The absence of cuprite (realizing the

danger of "absent mineral conclusions") is slightly anomalous since in order to move from the native copper field into that of malachite, it is necessary to cross the stability region of cuprite (fig. 11).

The absence of cuprite may be explained in three ways. A very rapid increase in P_{O_2} from 10^{-55} atm to 10^{-35} atm would eliminate the stability region of cuprite (Garrels, 1960, p. 88) as would a large total carbonate concentration (fig. 11). Also if no preserving medium such as gypsum were available cuprite would alter to malachite leaving no trace of its former existence.

The formation of malachite represents the most recent and presently prevailing conditions within the fault. The small amount of pyrite noted in the clayey gouge of this fault is apparently insufficient to contribute significantly to the acidity of the system.

Any attempt to arrive at Eh and pH conditions presently prevailing is confounded by the fact that the stability of the available "indicators" does not involve a change in valence and consequently is Eh independent.

Some work was done on the acidity of the system, however, and the pH was calculated with apparent success. Figure 14 shows the stability region of goslarite relative to zincite and sphalerite when total sulfur = 10^{-1} . Figure 14 was then superimposed upon figure 11 showing the stability range of malachite under similar conditions. Equilibrium

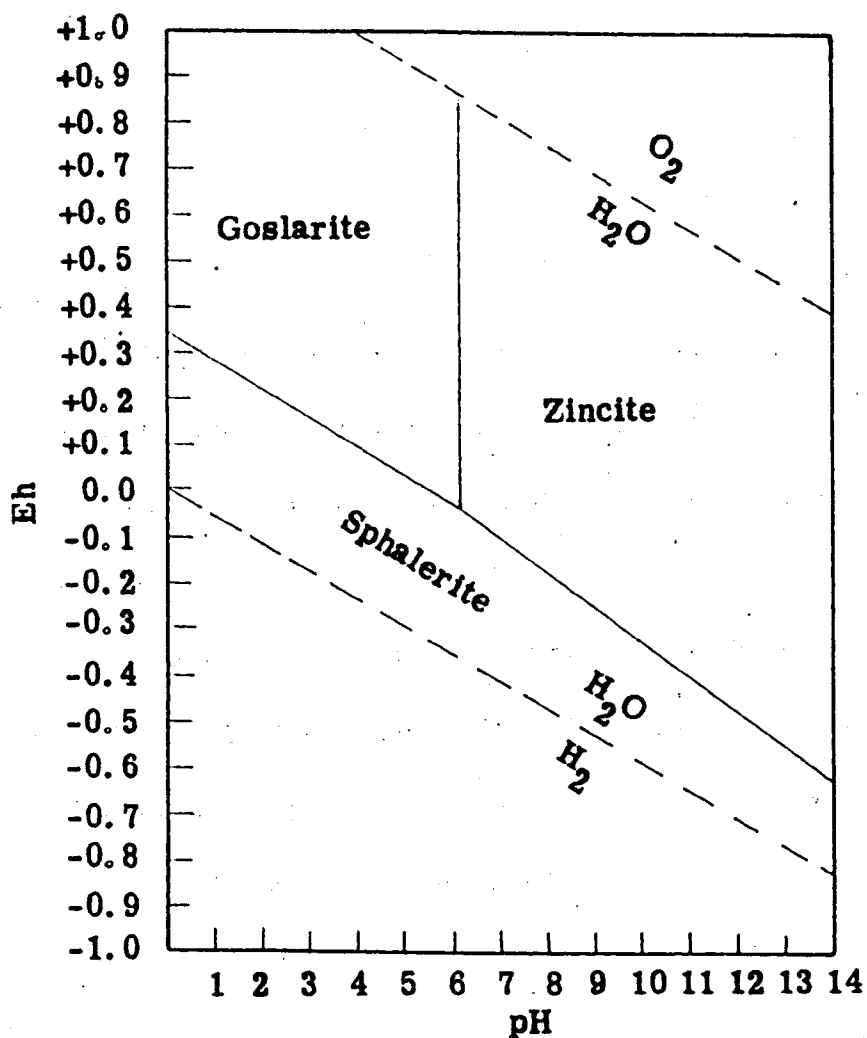


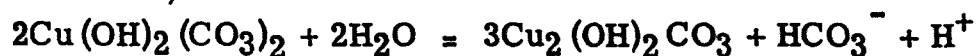
Figure 14. --Stability relations of some zinc minerals at 25°C, 1 atmosphere total pressure in the presence of water. Total S = 10⁻¹. Modified from Schmidt (1962).

of these two minerals with this environment is reasonably certain in view of the excellent unreacted crystals of the minerals found in contact. The area of mutual stability of goslarite and malachite is shaded in figure 15.

The area of mutual stability is an extremely narrow region between $\text{pH} = 5.9$ and $\text{pH} = 6.2$, but the Eh is only vaguely defined as lying somewhere between the upper stability boundary of sphalerite and the upper boundary of water stability.

The apparent absence of azurite provides a second method of arriving at the pH conditions discussed above but again provides no information on Eh since no oxidation or reduction is involved.

Silman (in Schmidt, 1962) has shown that if sulfate activity = 10^{-1} and $\text{pH} = 6$, $\log \sum \text{CO}_3$ must be no less than -1.75 if azurite is to be unstable in the system. Writing the azurite to malachite reaction as



$$\Delta F_R^0 = +11.22 \text{ Kcal/mole}$$

$$\Delta \log k = -8.23 = -\text{pH} + \log[\text{HCO}_3^-]$$

and substituting the minimum value of $\log [\text{HCO}_3^-] = -1.75$, we get a pH of 6.48, which is in good agreement with the pH range 5.9 to 6.2 obtained on the basis of goslarite-malachite equilibrium. However, only a range of Eh is available owing to the nature of the relationships between indicators.

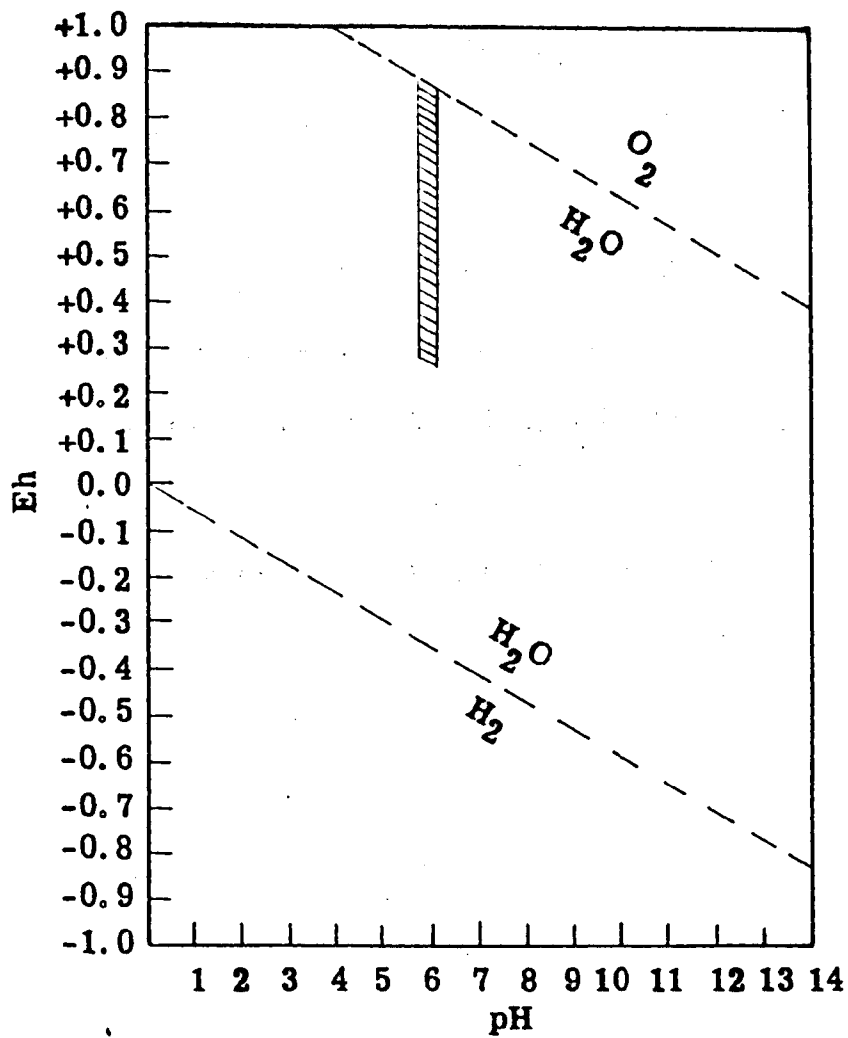


Figure 15. --Mutual stability field of goslarite and malachite at 25°C, 1 atmosphere total pressure. Total S = 10^{-1} .

Various other mineral species are present in the stope including rosasite, aurichalcite, calcite, and hematite. These minerals offer no help in determining oxidation-reduction potential, however, because their association with goslarite and malachite is only proximal and does not imply equilibrium. Observational evidence suggests that many of the species noted in the 100-foot level stope are related to very small fissures and carbonate ground waters moving in them rather than to the fault in which malachite and goslarite occur.

SUMMARY

The geology of the San Xavier West mine is typical of the pyrometasomatic deposits of the Pima mining district. Mineralization is structurally controlled and accompanied by rather intense garnetization of the carbonate host rock. Primary mineralization consists of galena, chalcopyrite, and sphalerite emplaced in a shattered green garnet in the order mentioned.

Supergene mineralogy is primarily zincian in character because of the relative abundance of that cation in the primary ore and because of "sealing" of primary lead and copper minerals within the garnet host by late-forming sphalerite.

Both the primary and secondary mineralogy are closely related to faults and fault systems, and faults represent the most promising areas for mineral study and collection.

Despite the small amount of pyrite associated with primary ore, some enrichment appears to have taken place to form steely chalcocite. The chemical environment can be traced from the reducing environment, where chalcocite formed through an increase in oxidation potential, to the present highly oxidizing environment, in which malachite is replacing chalcocite.

The most abundant secondary mineral, and that in which most of the zinc is held, is goslarite. This mineral appears to have formed directly from solution—upon the clayey gouge of one of the large south-dipping faults. Apparent equilibrium of goslarite with malachite indicates a prevailing pH of 6 to 6-1/2 with an oxidation potential less well defined but lying in the range 0.3 to 0.8.

In a large fault, best observed on the 150-foot level and representing the only area of extensive pyrite development, conditions are much more acidic. Evidence of high acidity is the apparent equilibrium between chalcantite and melanterite.

In this zone pH is apparently less than 3, and the oxidation potential is 0.3 to 0.6. The highly acidic conditions result from the movement of water through a zone containing abundant pyrite and almost no reactive carbonate material.

Small faults and fissures within the limestone country rock lack primary mineralization. These fractures represent a system initially open to CO₂ and since deprived of contact with the atmosphere. Garrels' work (1960) has shown that such a system is somewhat alkaline, having a pH of 9.9. In the San Xavier West mine, these fractures have yielded calcite, rosasite, hemimorphite, and malachite—supporting evidence for the slight alkalinity of the environment.

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