AN INVESTIGATION OF THE MANNER AND TIME OF FORMATION OF MALACHITE

by

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ABSTRACT

A group of minerals typical of the oxidation zone of copper deposits was studied using chemical thermodynamics, mineral stability relationships, and petrography. It has been concluded that many processes, such as alteration, can be explained using thermodynamics and are compatible with natural relationships.

A mineral assemblage consisting of basic carbonates of copper and zinc was investigated with carbon isotopes and mineral stability relationships. The results obtained are consistent with processes resulting from oxidation and leaching of a sulfide deposit followed by redeposition of copper and zinc in the zone of oxidation.

Four processes have been suggested by which copper could be introduced into a near-surface environment from depth. Reactions which would occur under these conditions may result in formation of mesogene or hypogene malachite and chrysocolla. A vein deposit containing minerals typical of the zone of oxidation was investigated and it has been concluded that the minerals may have formed from a hydrothermal solution related to near-surface volcanism.
INTRODUCTION

Minerals containing the cupric ion are generally highly diagnostic due to their green or blue color. This fact has given rise to the general term "green copper minerals," a necessary generalization because of the large number of minerals in this group, most of which are not readily distinguished from one another.

The cupric ion combines with many anions, forming such compounds as $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (malachite), $\text{Cu}_4(\text{OH})_6\text{SO}_4$ (brochantite), $\text{Cu}_2(\text{OH})\text{PO}_4$ (libethenite), and $\text{CuSiO}_3\cdot\text{H}_2\text{O}$ (dioptase). These compounds may be hydrated to various degrees as in langite which is brochantite with 1.5 water molecules. Using combinations of $\text{Cu}^{++}$ with anions such as $\text{CO}_3^{2-}$, $\text{PO}_4^{3-}$, $\text{SO}_4^{2-}$, $\text{AsO}_4^{3-}$, $\text{Cl}^-$, and $\text{OH}^-$ with various degrees of hydration, it can be seen that a large number of compounds might be formed. The situation is further complicated by various ratios of the ions involved as in malachite and azurite which have $\text{Cu}^{++}/\text{CO}_3^{2-}$ ratios of 2/1 and 3/2 respectively. In addition, other cations may accompany copper such as zinc in rosasite, lead in duftite, and calcium in conichalcite. The two things these minerals generally have in common, however, is the cupric ion and a resulting green or blue color.

When a sulfide ore body is exposed to oxidation (as a result of weathering processes), the unstable sulfides undergo various reactions. The reaction products are then either removed from the system or they react, under the new conditions, to form new minerals which
are stable. If a new mineral is formed, it is ideally a stable product of the reaction between the original sulfide minerals undergoing oxidation, the dissolved material in ground and meteoric waters, and the host rock containing the sulfides. Because of the abundance of the carbonate ion in both meteoric and ground waters and the abundant rock-forming carbonates, it might be expected that a common group of minerals resulting from the oxidation of sulfide ore bodies would be the metal carbonates. Accordingly, malachite is commonly present in varying degrees in portions of the oxidation zone of copper sulfide ore bodies.

Malachite is found in a wide variety of occurrences, the most common of which is a surface stain on rocks which previously contained copper sulfides. In the Rhodesian Copperbelt and Katanga, malachite forms hard botryoidal crusts banded with tenorite. The Emerald Isle mine in northwestern Arizona is in a conglomerate cemented by malachite, tenorite, and chrysocolla. Organic remains are replaced by malachite in the Silver Reef District, Utah. The Navajo sandstone, normally cemented by calcite, has a malachite cement at the White Mesa mine near Page, Arizona. Large crystals of malachite are rare, but at Bisbee, Arizona, large crystals of azurite are partially or completely replaced by malachite. At the Silver Hill mine near Silverbell, Arizona, earthy malachite veins up to 6 inches in width occur. Malachite is found as films on copper coins and pipes in humid regions, indicating its rapid rate of formation.

Malachite and related copper minerals such as azurite and chrysocolla are generally thought to form only as secondary minerals resulting from the oxidation of primary copper sulfides. A few authors,
such as Thomas (1949) in a discussion of the Emerald Isle mine, have suggested that these minerals might be primary.

It was my purpose to study, in detail, the factors governing the formation and stability of malachite and related minerals. By studying these factors I hoped to better understand the relationship between these minerals and the environments in which they occur. The study of malachite was carried out in two basic categories:

1. Chemical and instrumental analyses to determine some of the intensive variables concerning the mineral. The instrumental methods used were DTA and IR. These methods were used to study the temperature of dissociation of malachite and the manner in which this dissociation occurs. An attempt was also made to develop a method of cataloging malachite specimens based on IR spectra.

2. An investigation of some natural occurrences of malachite and associated minerals, done chiefly with chemical thermodynamics and petrography. One of these occurrences consists of a mineral assemblage typical of the oxidation zone of a deposit containing copper sulfides. Another occurrence studied, however, showed evidence of having formed by hydrothermal processes.

In addition, I have attempted to construct a geologic model compatible with field and laboratory data which would permit hydrothermal deposition of malachite and other such minerals which are now regarded only as secondary.
CHEMICAL ANALYSES

Malachite has a characteristic green color and can be readily identified by the release of CO\textsubscript{2} upon addition of dilute HCl. It belongs to the monoclinic crystal system. Malachite is commonly pure Cu\textsubscript{2}(OH)\textsubscript{2}CO\textsubscript{3}, but it appears to be able to incorporate considerable amounts of zinc and possibly calcium. A sample of zincian malachite from Bisbee, Arizona, contained 3.3\% ZnO (Table 1, number 6). The water and CO\textsubscript{2} content appear to vary up to 0.3\%. Analyses of seven malachite samples are shown in Table 1, numbers 1-7.

Azurite, like malachite, is monoclinic and effervesces with HCl, but has a deep blue color. Modern analyses are lacking, but the composition calculated from the formula Cu\textsubscript{3}(OH)\textsubscript{2}CO\textsubscript{3} is given in Table 1, number 8.

There are a number of basic carbonates of zinc and copper, but only two of these, rosasite and aurichalcite, have been substantiated as valid minerals. Two other compounds, paraaurichalcite-II and cuprozincite may prove to be equivalent either to rosasite or the zincian malachite mentioned above. Analyses of these compounds appear as numbers 9 through 17 in Table 1.

Chukhrov and Anosov (1950) have shown chrysocolla to be similar to minerals of the montmorillonite group. Medmontite or cupiferous beidellite was found to contain copper partially replacing aluminum in the octahedral position of beidellite. The sum of copper and aluminum in the octahedral position \( \sum Cu_0 + Al_0 \) is close to the sum of
### Table 1—Chemical analyses of basic carbonate minerals of copper and copper-zinc.

Analyses from Palache, Berman, and Frondel, 1951, pp. 249-268, except numbers 6 and 7, done by Hawley & Hawley, Tucson, Arizona.

<table>
<thead>
<tr>
<th>Number</th>
<th>Mineral</th>
<th>CuO</th>
<th>ZnO</th>
<th>PbO</th>
<th>CaO</th>
<th>H₂O</th>
<th>CO₂</th>
<th>Cu/Zn</th>
</tr>
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<tr>
<td>1</td>
<td>malachite</td>
<td>72.0</td>
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<td>-</td>
<td>-</td>
<td>8.2</td>
<td>19.9</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>malachite</td>
<td>71.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.2</td>
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<td>-</td>
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<tr>
<td>3</td>
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<td>tr</td>
<td>-</td>
<td>8.4</td>
<td>19.9</td>
<td>154</td>
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<td>-</td>
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<td>8.2</td>
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<td>72.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.1</td>
<td>20.0</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>19.5</td>
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<td>0.2</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>159</td>
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<td>8</td>
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<td>-</td>
<td>-</td>
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<td>25.5</td>
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<td>-</td>
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<td>1.9</td>
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<td>12</td>
<td>aurichalcite</td>
<td>19.9</td>
<td>54.1</td>
<td>-</td>
<td>-</td>
<td>9.9</td>
<td>16.1</td>
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<td>-</td>
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<td>-</td>
<td>9.5</td>
<td>18.4</td>
<td>1.5</td>
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<tr>
<td>17</td>
<td>cuprozinicite</td>
<td>58.6</td>
<td>12.7</td>
<td>-</td>
<td>-</td>
<td>7.6</td>
<td>19.7</td>
<td>4.5</td>
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ions in octahedral position typical of magnesian montmorillonites. Com­
positions of selected chrysocolla samples (Chukhrov and Anosov, 1950)
are shown in Table 2.

TABLE 2.—Stoichiometric analyses of selected chrysocolla samples
showing (Al,Cu) in octahedral sites and (Al, Si) in tetrahedral sites
(Chukhrov and Anosov, 1950).

<table>
<thead>
<tr>
<th>sample number</th>
<th>octahedral site</th>
<th>tetrahedral site</th>
<th>O</th>
<th>OH</th>
<th>( \sum \text{Cu}_6^+ + \text{Al}_6^- )</th>
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<tr>
<td>1</td>
<td>0.36 2.53</td>
<td>0.47 3.53</td>
<td>10</td>
<td>2</td>
<td>2.89</td>
</tr>
<tr>
<td>2</td>
<td>0.23 2.56</td>
<td>0.14 3.86</td>
<td>10</td>
<td>2</td>
<td>2.79</td>
</tr>
<tr>
<td>3</td>
<td>0.85 1.76</td>
<td>0.42 3.58</td>
<td>10</td>
<td>2</td>
<td>2.61</td>
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<tr>
<td>4</td>
<td>0.78 1.88</td>
<td>0.44 3.56</td>
<td>10</td>
<td>2</td>
<td>2.66</td>
</tr>
<tr>
<td>5</td>
<td>0.66 2.97</td>
<td>0.44 3.56</td>
<td>10</td>
<td>2</td>
<td>3.03</td>
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</table>

Table 2 shows that at constant silica content the Cu:Al ratio
can vary (numbers 4 and 5) and that the Si:Al ratio can vary at constant
copper content (numbers 1 and 2).
Gröger (1900), working with the system Cu-H₂O-CO₂, found that aqueous solutions of CuSO₄ mixed with Na₂CO₃ formed a light bluish-green precipitate which turned green as CO₂ was given off. The final precipitate proved to be 3Cu₂(OH)₂CO₃·H₂O. Free (1908) worked further in this system concluding that precipitated copper carbonates form an unstable series of compounds or are solid solutions of indefinite composition, and that by bubbling CO₂ through these solutions, the copper carbonates change to a stable compound. He also found that as the CO₂ concentration increased, the solubility of precipitated basic copper carbonate increased, but that the presence of either Na₂CO₃ or CaCO₃ greatly decreased the solubility.

The author introduced aqueous solutions of copper acetate into solutions of K₂CO₃. A green precipitate formed near pH = 7, and as the pH was increased toward 11, the precipitates became increasingly blue in color. The light bluish-green precipitate obtained by Gröger (1900) appears to be due to an admixture of the unstable compound Cu(OH)₂ and malachite. As noted by Gröger above, precipitates became green as time progressed. The instability observed by Free may have been due to re-solution of the Cu(OH)₂ which also removed the blue color from the precipitate. Newberg (1967) describes an "aging" process by which amorphous precipitates of copper compounds change with time to stable crystalline species. One such reaction described is the "aging" of amorphous Cu(OH)₂ to crystalline tenorite. The color change
observed by Gröger above may be a similar "aging" process for malachite.

Malachite appears to be stable at temperatures up to the boiling point of water in solutions of $10^{-1}$ to $10^{-3}$ M $K_2CO_3$ and pH values from 7 to 11. Azurite, however, decomposed to tenorite (CuO) at about 63°C in $10^{-1}$ M $K_2CO_3$. A sample of malachite and azurite was placed in a solution of $10^{-1}$ M $K_2CO_3$, and as the temperature was increased the azurite turned black, but the malachite remained unchanged.
IR AND DTA CHARACTERISTICS OF MALACHITE

Infrared Analysis

A discussion of infrared analysis (IR) appears in Appendix I. Eleven different malachite samples were analyzed using IR. The samples were chosen to represent: (1) a wide variety of environments, (2) similar habits from different locations, and (3) different habits from the same location. The samples are described in Table 3.

Of the eleven samples, the banded malachite samples showed the closest correspondence (Appendix I, Table 9) with the possible exception of sample K, which is the only malachite associated with chrysocolla. The best agreement is shown between samples G and I. The two crystalline samples from Bisbee, Arizona (samples E and F) show agreement on eight of the eleven peaks. The 815 and 745 cm\(^{-1}\) peaks of samples G, H, I, and J are the same; this peak probably corresponds to either the CO\(_3\)\(^{\text{=}}\) functional group to which all of the samples were standardized (1380 cm\(^{-1}\)) or a similar mode of origin of the samples.

Differential Thermal Analysis

Beck (1950) reports a loss of water from malachite at about 315\(^{\circ}\)C leaving tenorite. Small amounts of water are reported to be lost below 200\(^{\circ}\)C (Binder, 1937). According to Beck, azurite loses water at about 410\(^{\circ}\)C, also leaving tenorite. Rose (1851), however, reports a much lower decomposition temperature for azurite.
TABLE 3.—Description of malachite samples used in IR analysis


B. Earthy vein-filling malachite in large masses, Silverbell, Arizona.

C. Malachite oxidation crust on limestone, southern Dragoon Mountains, Arizona.

D. Malachite oxidation crust, Butte, Montana.

E. Fibrous clusters of zincian malachite, Bisbee, Arizona.

F. Crystalline malachite after azurite, Bisbee, Arizona.

G. Malachite banded with tenorite, Bisbee, Arizona.

H. Malachite banded with tenorite, Tsumeb, S.W. Africa.

I. Malachite banded with tenorite, Katanga, Belgian Congo.

J. Small spherules of banded malachite and tenorite forming botryoidal crust on alaskite, Bagdad, Arizona.

K. Malachite banded with tenorite, capped with crust of chrysocolla, Brazil.
The malachite and azurite used for differential thermal analyses (DTA) were from the Silver Hill mine, Silverbell, Arizona. The instrument was standardized with the $\alpha-\beta$ quartz transition which occurred at $575^\circ C$ (Figure 1, d) and smithsonite from Kelly, New Mexico (Figure 1, c) which agreed with published values (Figure 1, a and b) (Kerr and Kulp, 1948).

Malachite and azurite were then analyzed, giving the following results:

1. Malachite heated to $200^\circ C$ and held at that temperature for 12 hours turned dark, but still gave the malachite IR pattern.
2. The DTA pattern for malachite showed a double endotherm (Figure 1, e). Azurite behaved in the same manner, showing two endotherms (Figure 1, f).
3. The infrared pattern for malachite heated to $350^\circ C$ shows an absorption peak at $1400 \text{ cm}^{-1}$, typical of simple carbonates, and a transmission peak at $650 \text{ cm}^{-1}$ similar to tenorite (Figure 12, c).

In order for these two basic carbonates of copper to decompose to tenorite, not only must there be a loss of $\text{H}_2\text{O}$, but also of $\text{CO}_2$.

Malachite would decompose according to

$$\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2.$$  \hspace{1cm} (1)

If the $\text{H}_2\text{O}$ and $\text{CO}_2$ are lost at different temperatures, there will be one of two reactions which occur first: either

$$\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow \text{Cu}($$OH$)_2 + \text{CO}_2 + \text{CuO} \hspace{1cm} (2)$$

or

$$\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow \text{CuCO}_3 + \text{H}_2\text{O} + \text{CuO}.$$ \hspace{1cm} (3)

The compound $\text{Cu}($OH$)_2$ is very unstable and decomposes readily to CuO.
Figure 1. Thermal Curves for Smithsonite, Quartz, Malachite, and Azurite
with gentle heating. The compound CuCO₃, according to Sneed, Maynard, and Brasted (1953), has not been isolated.

Malachite heated to 350°C (just below the second endotherm) was analyzed by IR. The compound showed a broad absorption peak at 1390 cm⁻¹ corresponding to ionic carbonate, another such peak at 1025 cm⁻¹ corresponding to covalent carbonate, and a transmission peak corresponding to tenorite (Figure 11, e). When heated to 400°C, malachite showed an IR pattern identical to CuO.

The double endotherms of malachite and azurite are indicative of the loss of H₂O and CO₂ at different temperatures.

IR analysis indicates that after the first endotherm of malachite at 240°C, a compound develops containing ionic carbonate and copper oxide. Above the second endotherm, the only compound present was copper oxide. Malachite, therefore, appears to decompose in two steps; the first step involves a loss of water, and the second corresponds to a loss of CO₂ as shown in Equation 4.

\[
\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow \text{CuCO}_3 + \text{CuO} + \text{H}_2\text{O} \rightarrow 2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O} \quad (4)
\]

Summary and Conclusions

A brief investigation of certain carbonates, oxides and basic carbonates has shown that infrared analysis may be useful as a qualitative tool for identification, indication of mode of origin, and determination of impurities in these minerals. In order to make a definite conclusion, however, a large number of malachite samples should be run with particular attention to type of host rock, habit, and mode of origin. This
work should be accompanied by quantitative analyses for Cu, Zn, Pb, Ca, CO$_3^{2-}$, and H$_2$O.

Differential thermal analysis indicates that malachite and azurite decompose in two steps. Malachite appears to lose water first, followed by loss of CO$_2$. The intermediate compound in this decomposition may be the compound CuCO$_3$, which has otherwise not yet been synthesized.
ALTERATIONS INVOLVING MALACHITE

Many secondary copper minerals are replaced by malachite, among them chalcocite, chrysocolla, and azurite. Malachite is also replaced by other secondary minerals such as chrysocolla and tenorite. In addition, malachite is frequently found intergrown with tenorite, chrysocolla, azurite, cuprite, and other such minerals. Intergrowth of copper minerals is frequently attributed to coprecipitation which in most instances involves precipitation on a phase boundary. The commonness of such occurrences makes this situation appear to be commonplace, in spite of the low probability of a system being exactly on a phase boundary. Three common two-phase systems will be investigated using chemical thermodynamics and ionic equilibria.

Silman (1958), Rossini et al. (1952), and Latimer (1952) have determined the existence of cupric ions other than \( \text{Cu}^{++} \) in the system \( \text{Cu}-\text{H}_2\text{O}-\text{CO}_2 \). These ions are \( \text{CuCO}_3^0 \), \( \text{Cu(CO}_3)_2^- \), \( \text{HCoO}_2^- \), and \( \text{CuO}_2^- \). Using free energy data from Appendix V, the stability fields of these ions can be determined as a function of pH and \( \sum \text{CO}_2(aq) \). These fields are shown in Figure 2.

Banded Malachite and Tenorite

Alternate black and green layerings of malachite and tenorite on the order of a millimeter in width are found in natural mineral specimens. These minerals form thick encrustations from such places as Katanga, Rhodesia, Tsumeb, South West Africa, and Bisbee, Arizona. The apparent
Figure 2. Stability of Ions in the System Cu-H$_2$O-CO$_2$
explanation for such banding is the fact of deposition while the carbonate concentration fluctuates about the phase boundary between the two minerals under consideration (Equation 5).

\[2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2(\text{OH})_2\text{CO}_3\]  \hspace{1cm} (5)

Figure 3 shows this phase boundary to be $10^{-3.8}$ atmospheres of CO$_2$.

The phase rule applied to this intergrowth requires three degrees of freedom (F). There are two phases (P): malachite $(2\text{CuO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O})$ and tenorite (CuO). These minerals are made up of three components (C): CuO, H$_2$O, and CO$_2$. Therefore, using the phase rule:

\[P + F = C + 2 \]
\[F = C - P + 2 \]
\[= 3.\]

Table 4 presents analyses of ground water samples from limestone and quartz monzonite. It can be seen from Figure 2 that for both of these samples, the dominant ionic species of copper and carbonate are CuCO$_3^0$ and HCO$_3^-$ respectively. The stability of the CuCO$_3^0$ and HCO$_3^-$ ions means that in these environments the dissociation of malachite is not that shown in Equation 6 but rather is that shown in Equation 7.

\[\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightarrow 2\text{Cu}^{++} + 2(\text{OH}^-) + \text{CO}_3^-\]  \hspace{1cm} (6)
\[\text{Cu}_2(\text{OH})_2\text{CO}_3 + \text{HCO}_3^- \rightarrow 2\text{CuCO}_3^0 + \text{H}_2\text{O} + (\text{OH}^-)\]  \hspace{1cm} (7)

A significant point of the relationship shown in Equation 7 is the fact that increasing HCO$_3^-$ activity favors solution rather than deposition of malachite.
Figure 3. Stability of Selected Copper Minerals in Water

Minerals are plotted as a function of \( P(O_2) \) and \( P(CO_2) \) at 25°C and 1 atmosphere total pressure (after Garrels and Christ, 1965).
TABLE 4.--Partial composition of ground-water samples
Recalculated from Hem (1959).

<table>
<thead>
<tr>
<th>ion</th>
<th>ppm</th>
<th>log m*</th>
<th>ppm</th>
<th>log m*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_3^-$</td>
<td>24</td>
<td>-3.5</td>
<td>95</td>
<td>-2.9</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>513</td>
<td>-1.7</td>
<td>72</td>
<td>-2.5</td>
</tr>
<tr>
<td>K$^+$</td>
<td>23</td>
<td>-3.2</td>
<td>2.4</td>
<td>-4.2</td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>264</td>
<td>-1.9</td>
<td>1.3</td>
<td>-4.2</td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>79</td>
<td>-2.2</td>
<td>0.3</td>
<td>-4.6</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>964</td>
<td>-1.8</td>
<td>58</td>
<td>-2.8</td>
</tr>
<tr>
<td>SO$_4^{=}$</td>
<td>147</td>
<td>-2.5</td>
<td>32</td>
<td>-3.2</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>815</td>
<td>-1.6</td>
<td>6.5</td>
<td>-3.7</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.2</td>
<td>-5.0</td>
<td>16</td>
<td>-3.1</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td></td>
<td></td>
<td>9.4</td>
</tr>
<tr>
<td>T (°C)</td>
<td>21</td>
<td></td>
<td>54</td>
<td></td>
</tr>
</tbody>
</table>

*m = molality of ion.


The two environments of Table 4, the limestone (Case 1) and the quartz monzonite (Case 2), will be discussed with respect to the malachite-tenorite intergrowth.

**Case 1.** In order that a copper mineral may be precipitated in ground water from the limestone environment of Table 4, the CuCO$_3^0$ activity must be greater than about $10^{-5.5}$ (Figure 4, point A). Under these conditions, the first precipitation curve encountered is that of malachite, so this mineral should precipitate. The resulting copper activity after precipitation of malachite should be $10^{-5.5}$ as determined by Equation 7. Using the pH and $\alpha$(HCO$_3^-$)\* conditions of this system, Equation 8 can be used to determine the CuCO$_3^0$ activity required for equilibrium between malachite and tenorite.

$$2\text{Cu}_2\text{(OH)}_2\text{CO}_3 \rightleftharpoons 3\text{CuO} + \text{H}_2\text{O} + \text{HCO}_3^- + \text{CuCO}_3^0 + \text{H}^+ \quad (8)$$

$$K_{eq} = 10^{-18.1} = (\text{CuCO}_3^0) (\text{H}^+) (\text{HCO}_3^-)$$

$$\text{(CuCO}_3^0) = 10^{-9.8}$$

The resulting copper ion activity after precipitation of malachite is more than sufficient to maintain malachite as the stable phase. It can be concluded, therefore, that in the limestone environment discussed, malachite should precipitate and remain stable.

**Case 2.** In order for malachite to precipitate in the quartz monzonite environment (Figure 4, point B), copper must have an activity greater than or equal to $10^{-6.9}$. Precipitation of malachite in this environment results in $\alpha$(CuCO$_3^0$) = $10^{-7.4}$. The equilibrium $\alpha$(CuCO$_3^0$) for the pH and $\alpha$(HCO$_3^-$) of this environment is calculated to be $10^{-5.9}$.

* The symbol $\alpha(\cdot)$ will be used throughout the text to indicate the ionic activity of the species in parentheses.
Figure 4. Precipitation Curves for Malachite and Tenorite

Shaded side of line indicates solid phase.
in the same manner as in Case 1. The \( a(CuCO_3^0) \) resulting from precipitation of malachite in this system, therefore, is insufficient to support malachite as a stable solid.

Malachite will be the first mineral to precipitate if the original copper activity is greater than \( 10^{-6.9} \). But unless the copper ion activity is maintained above \( 10^{-5.9} \), the malachite will alter to tenorite under equilibrium conditions. In other words, if the quartz monzonite system were closed after the initial introduction of copper, the precipitation of malachite makes malachite unstable with respect to tenorite.

In the system described by Case 2, a constant recharge of copper to the system may maintain the copper ion activity at a value high enough to keep malachite stable. If, however, there is a period in which there is no recharge of copper, the malachite should begin altering to tenorite. This alteration should begin at the surface of malachite in contact with the solution and progress downward into the malachite. When new copper is brought into the system, malachite should again precipitate and essentially seal the lower minerals off, halting the alteration process. When copper recharge again ceases, this alteration process begins again in the new malachite.

The resulting mineral assemblage should show a sharp malachite-tenorite boundary where new malachite precipitated on the tenorite formed by alteration. This band of tenorite should progress downward into the malachite which is being altered and gradually blend into unaltered malachite. This would form a band of tenorite with a sharp boundary against malachite on one side, and gradational boundary into malachite on the other side. A photograph of a banded malachite-tenorite
assemblage from Tsumeb, S.W. Africa, shows this to be the case (Figure 5). The tenorite appears to have formed as needles perpendicular to the banding, but these needles blend into malachite showing the tenorite to be pseudomorphic after malachite.

This type of alteration can occur quite rapidly. Azurite precipitated in a 250 ml flask from a solution of $10^{-2} \text{ M } \text{HCO}_3^-$ at pH = 7, and covered the bottom of the flask with a film one or two mm thick. The flask was then heated to 85°C until all of the azurite decomposed to tenorite. Both minerals were identified by X-ray analysis. The flask was then cooled, sealed, and left to stand. After one day the tenorite had a green surface coating, and by the end of three days, the tenorite had altered completely to malachite. The azurite probably decomposed according to

$$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2 \rightarrow \text{CuO} + 2\text{CuCO}_3 + \text{H}_2\text{O},$$

(9)

and the tenorite then altered by reversing Equation 3.

As has been shown, stability between malachite and tenorite depends not only on the carbonate ion activity but also on pH and copper ion activity, giving the three degrees of freedom predicted by the phase rule. Equilibrium between malachite and tenorite is expressed by

$$2\text{Cu}_2(\text{OH})_2\text{CO}_3 \rightleftharpoons 3\text{CuO} + \text{H}_2\text{O} + \text{HCO}_3^- + \text{CuCO}_3^0 + \text{H}^+.\quad (10)$$

Pseudomorphs of Malachite after Azurite

Azurite is frequently found altered to malachite, with malachite retaining the azurite crystal form. Large crystals of malachite pseudomorphs after azurite are common at Bisbee, Arizona, and Tsumeb, S.W. Africa. The reverse transition of malachite altering to azurite is rare.
Figure 5. Malachite banded with tenorite, Tsumeb, S.W. Africa (polished section, X180; malachite, green; tenorite, black).
The malachite formed by this alteration consists of radiating clusters of needles extending from the original surface of the azurite crystal down into the azurite.

The alteration of azurite to malachite can be explained as accompanied by a decrease in $P(CO_2)$ shown by Figure 3 or carbonate activity and pH (Equation 11).

\begin{align*}
2Cu_3(OH)_2(CO_3)_2 + 2H_2O & \rightleftharpoons 3Cu_2(OH)_2CO_3 + 2H^+ + CO_3^{2-} \quad (11)
\end{align*}

Ridge (1949) states that replacement equations must be balanced molecularly, volumetrically, and electrically. The above reaction (Equation 11) is balanced stoichiometrically and electrically but not volumetrically. The absolute volume ($V$) of a molecule is defined by

\begin{equation}
V = \frac{WZ}{0.6D} \quad (12)
\end{equation}

where $W$ is the molecular weight, $Z$ is the number of formula units in a cell, and $D$ is the density of the mineral. For malachite, $W = 221.11$ gm/mole, $Z = 2$, and $D = 4.0$ gm/cc; for azurite, $W = 344.66$ gm/mole, $Z = 2$, and $D = 3.88$ gm/cc. The molar volumes of malachite and azurite, therefore, are 184.0 cc/mole and 296.0 cc/mole respectively. The molar volume of azurite is about 61% (roughly $5/8$) larger than that of malachite.

If malachite were to replace azurite according to Equation 11, the volume would decrease by about 7% and distort the pseudomorph. In order to satisfy Ridge's requirements given above, the volume change must be rectified. This could be accomplished with Equations 13 and 14.

\begin{align*}
5Cu_3(OH)_2(CO_3)_2 + 6H_2O + CuCO_3^O & \rightarrow \\
8Cu_2(OH)_2CO_3 + 3HCO_3^- + 3H^+ \quad (13)
\end{align*}
\[
5\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2 + 6\text{H}_2\text{O} + \text{Cu}^{++} \rightarrow \\
8\text{Cu}_2(\text{OH})_2\text{CO}_3 + 3\text{H}_2\text{CO}_3 + 2\text{H}^+ 
\]

(14)

These reactions show the alteration process to be dependent on the activities of copper and carbonate ions and upon the pH.

The lack of pseudomorphs of azurite after malachite and the abundance of the reverse alteration is readily explained. If the activity of copper introduced into a system is greater than \(10^{-7.0}\), azurite is more likely to precipitate (Figure 6). Once it has precipitated, the stability region for azurite at moderate carbonate activities such as those found in most ground-water environments is very narrow (Figure 7), and the azurite is likely to alter to malachite. The sequence of azurite after malachite is also readily explained. Initial leaching solutions will be low in copper and are more likely to precipitate malachite. As oxidation increases and leaching becomes more intense, the copper activity increases and azurite will precipitate. Garrels and Dreyer (1952, p. 347) state that "... evidence indicates that most supergene solutions derived from the weathering of primary copper sulfides contain less than 0.001 mols \(\text{Cu}^{++}\) of copper ion per liter." This value is sufficient to retain azurite without alteration to malachite if azurite is precipitated first.

Associated Malachite and Chrysocolla

A common feature of oxidation zones in areas of copper mineralization is intergrown malachite and chrysocolla. Near Jerome, Arizona, botryoidal masses which consist of intergrown bands of malachite and chrysocolla can be found in gravels containing minerals precipitated by
Figure 6. Precipitation Curves for Malachite and Azurite

Shaded side of line indicates solid phase.
Figure 7. Stability of Azurite with Respect to Malachite in system Cu-H$_2$O-CO$_2$
copper leached from the massive sulfide body nearby. Garrels and Dreyer (1952) attribute this type of intergrowth to a delicate balance between the activity of silicate and carbonate ions. In the Jerome open pit, fine needles of malachite are found altered to pseudomorphs of chrysocolla.

Chrysocolla is found as coatings on limestone, indicating that factors other than the anion of the host rock may determine the formation of secondary minerals.

A small amount of azurite precipitated in the laboratory was left in a glass test tube in a solution with pH = 10 and a carbonate activity of $10^{-1.5}$; this carbonate activity is more than sufficient to maintain azurite stability. X-ray analysis at the end of two weeks indicated that the material in the test tube had a pattern similar to museum specimens of chrysocolla and that the azurite had presumably altered to blue chrysocolla. Thus, leaving a copper carbonate in the presence of silica at moderate pH values is one way in which chrysocolla might form in the zone of oxidation.

The veining and coating of limestone by chrysocolla rather than malachite might be explained by the pH of the environment. If the pH were acid, the copper silicate might form because conditions were too acidic to permit malachite stability. A more basic pH might permit the precipitation of chrysocolla because the system was too alkaline to dissolve any limestone to supply carbonate ions for formation of significant amounts of malachite.
Summary

Assemblages of secondary copper minerals can be shown to be dependent upon a number of factors. Intergrowth phenomena between two minerals depends not only upon anion ratios in the mineralizing solutions but also upon pH and activities of copper complexes. Factors which influence copper content in ground waters such as seasonal or long-range variations in rainfall may be just as important as the composition of the original ground water.

Chemical thermodynamics applied to systems permits certain processes to be predicted, and the validity of the predictions is borne out by field relationships. Thermodynamics indicates not only what mineral will form under given ground-water conditions but also what will happen to that mineral if the system is closed.
STUDY OF MALACHITE FROM THE SILVER HILL MINE

The Silver Hill mine is located in the Waterman Mountains, Pima County, Arizona, near a hydrothermally altered quartz monzonite porphyry. Within this igneous stock is the Silverbell open-pit copper mine operated by the American Smelting and Refining Company. Around the perimeter of the intrusion is a garnetiferous contact metasomatic zone in Paleozoic limestones.

McClymonds (1957) locates the Silver Hill mine in the Horquilla Formation of Pennsylvanian age and attributes the mineralization and accompanying silicification to Tertiary volcanic activity. One stope in this mine consists of pods and veins of malachite, azurite, tenorite, and rosasite in a host rock composed of massive to granular silica. Veins of malachite occur up to six inches thick and tens of feet in length enclosed in envelopes of kaolinite. Although most of the host rock appears to be silicified carbonate rocks, certain exposures show evidence of having been a limy sandstone from which the calcareous cement has been leached. The presence of crinoid stems in the silica suggests the original rock to be either lower Horquilla Formation or upper Escabrosa Limestone which has undergone mild alteration in the form of silicification and leaching.

In the stope under consideration, needles of malachite radiate from cores of intergrown malachite and tenorite. On the ends of the needles of malachite are tufts of rosasite. This assemblage is found
attached to a base of silica. These phenomena indicate the paragenesis to be:

<table>
<thead>
<tr>
<th>early</th>
<th>late</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica</td>
<td></td>
</tr>
<tr>
<td>tenorite</td>
<td></td>
</tr>
<tr>
<td>malachite</td>
<td></td>
</tr>
<tr>
<td>rosasite</td>
<td></td>
</tr>
</tbody>
</table>

The minerals were identified using X-ray diffraction.

**C\textsuperscript{14} Age Dating of Malachite**

Since malachite is a carbonate, it was thought that a recent origin of this mineral might be detected using radiocarbon age dating. Ages obtained with C\textsuperscript{14} are limited to a few tens of thousands of years before present. The significant period of time which could be studied using this method of age dating is the pluvial period which existed in Arizona 10-30 thousand years before present during the Wisconsin glacial period in North America. During this period the humid conditions necessary to form large veins of malachite would have existed. Otherwise, if large quantities of water were not available, the malachite would be immobilized as a surface stain.

The C\textsuperscript{14} content of the CO\textsubscript{2} of a sample of malachite obtained from the Silver Hill mine was counted in a 5-liter proportional counter at the University of Arizona Radiocarbon Laboratory. The method of calculation used to determine the C\textsuperscript{14} activity of the malachite sample is shown in Appendix II. This calculation shows the age of the malachite to be greater than 41,000 years before present and indicates that the
carbon in the malachite is older than the recent pluvial period.

$^{13}$C Analysis of Malachite

The $^{12}/^{13}$ ratio in a sample is partially indicative of the origin of the carbon in the carbonate. The $^{13}$C value for the Silver Hill malachite was -11.1 as determined by Dr. Austin Long at the Smithsonian Institute Radiocarbon Laboratory, Washington, D.C. This value is converted using the PD Belemnite standard to a $^{12}/^{13}$ ratio of 90.0. Table 5 shows the $^{12}/^{13}$ ratios for carbonate minerals from the oxidation zone of ore deposits and hydrothermal carbonate minerals.

A compilation of $^{12}/^{13}$ values for various types of carbonates (Table 6) shows the value determined for the Silver Hill mine to be typical of either values found in an oxidation zone or from metasomatic carbonates. Either of these environments could satisfy the conditions at the Silver Hill mine.

<table>
<thead>
<tr>
<th>Carbonate environment</th>
<th>$^{12}/^{13}$ range</th>
</tr>
</thead>
<tbody>
<tr>
<td>metasomatic</td>
<td>88.0 - 90.2</td>
</tr>
<tr>
<td>oxidation zone</td>
<td>89.2 - 90.7</td>
</tr>
<tr>
<td>hydrothermal</td>
<td>89.0 - 89.7</td>
</tr>
<tr>
<td>sedimentary</td>
<td>88.1 - 88.9</td>
</tr>
<tr>
<td>fresh water</td>
<td>88.0 - 89.8</td>
</tr>
</tbody>
</table>

Determination of Conditions of Deposition

Since the assemblage at the Silver Hill mine occurs in leached Horquilla limestone, the system should consist of an aqueous
### TABLE 5: $^{12}C/^{13}C$ ratios for oxidation zone and hydrothermal carbonates

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>$^{12}C/^{13}C$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zone of oxidation (Rankama, 1954)</strong></td>
<td></td>
</tr>
<tr>
<td>Malachite - Nizhne Tagilsk, Ural Mtns., U.S.S.R.</td>
<td>89.9</td>
</tr>
<tr>
<td>Malachite - Punta de Cobre, Atacama, Chile</td>
<td>89.4</td>
</tr>
<tr>
<td>Malachite - Burra Burra mine, Australia</td>
<td>89.6</td>
</tr>
<tr>
<td>Azurite - Chessy, France</td>
<td>89.7</td>
</tr>
<tr>
<td>Azurite - Solotushinsk, Kolyvan, U.S.S.R.</td>
<td>89.3</td>
</tr>
<tr>
<td>Azurite - Burra Burra mine, Australia</td>
<td>89.6</td>
</tr>
<tr>
<td>Cerussite - Leadhills, Scotland</td>
<td>90.7</td>
</tr>
<tr>
<td>Cerussite - Broken Hill, Australia</td>
<td>90.2</td>
</tr>
<tr>
<td><strong>Hydrothermal carbonates (Rankama, 1963)</strong></td>
<td></td>
</tr>
<tr>
<td>Calcite - Kongsberg, Norway</td>
<td>89.2</td>
</tr>
<tr>
<td>Calcite - Kongsberg, Norway</td>
<td>89.6</td>
</tr>
<tr>
<td>Calcite and dolomite - alpine fissure fillings,</td>
<td>89.0 - 89.2</td>
</tr>
<tr>
<td>Switzerland, 20 samples, range</td>
<td></td>
</tr>
<tr>
<td>Calcite and aragonite - 5 samples, range</td>
<td>89.0 - 89.2</td>
</tr>
</tbody>
</table>
mineralizing solution reacting with CaCO₃. The intergrown malachite and tenorite could be due to alteration of the type discussed in the last chapter or to precipitation on or about the malachite-tenorite phase boundary (P CO₂ = 10⁻³.₈ atm). Intergrowth as a result of coprecipita-

tion will be assumed because no evidence of pseudomorphs indicating alteration were evident. The ions necessary for the formation of malachite and tenorite are: Cu⁺⁺, OH⁻, CO₃⁻, H⁺, HCO₃⁻, and H₂CO₃O; in addition, Ca⁺⁺ was probably present initially in the host rock. Equi-

librium calculations can be used to determine the concentrations of the various ions in solution at the time of deposition (Appendix III). The assumptions made in the calculations are:

1. The minerals which determine the equilibrium are calcite, malachite and tenorite.

2. The aqueous carbonate ions are of high enough concentration to be unaffected by the precipitation of malachite.

3. Water, calcite, malachite, and tenorite are continuous phases with activities = 10⁰.

The activities of the ions determined by this method are shown in Column 1 of Table 7.

It could be assumed, however, that calcite was not present at the time of formation of the malachite. This absence would be the case if calcite had been removed from the calcareous host rock by an earlier process such as silicification related to contact metamorphism. Under these conditions calcite would not affect the equilibrium, and the Ca⁺⁺ ion might not be present in amounts significant enough to be used in Equation 41 of Appendix III. The activities of ions calculated using
this modification are shown in Column 2 of Table 7.

TABLE 7.—Theoretical ionic activities calculated with thermodynamics

<table>
<thead>
<tr>
<th>ion</th>
<th>log activity</th>
</tr>
</thead>
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<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Ca^{++}</td>
<td>-3.3</td>
</tr>
<tr>
<td>Cu^{++}</td>
<td>-8.8</td>
</tr>
<tr>
<td>OH^-</td>
<td>-5.5</td>
</tr>
<tr>
<td>H^+</td>
<td>-8.5</td>
</tr>
<tr>
<td>HCO_3^-</td>
<td>-3.2</td>
</tr>
<tr>
<td>CO_3^-</td>
<td>-5.2</td>
</tr>
<tr>
<td>H_2CO_3^0</td>
<td>-5.3</td>
</tr>
</tbody>
</table>

1. $P(CO_2) = 10^{-3.8}$ atm with malachite, calcite, and water.
2. $P(CO_2) = 10^{-3.8}$ atm with malachite and water.
3. System open to atmospheric $CO_2$ and closed before addition of $CaCO_3$ (Garrels and Christ, 1965).
4. Pure water in equilibrium with $CaCO_3$ (Garrels and Christ, 1965).

The values calculated by Garrels and Christ (1965) for a system of water originally open to atmospheric $CO_2$ then closed before addition of $CaCO_3$ and a system of $CaCO_3$ in pure water are shown in Columns 3 and 4 of Table 7 respectively.

If the conditions represented by Column 1 were those that prevailed, the initial solution introduced into the limestone must have had a fairly low pH because this system has a higher concentration of $Ca^{++}$ and $HCO_3^-$ than those of Column 3. A lower pH would dissolve more
CaCO₃, thus increasing the Ca⁺⁺ and HCO₃⁻ concentrations. The pH in Column 1 is very close to that measured by Sato (1960) for oxidized ore in limestone at Bisbee, Arizona (pH = 8.3). The carbonate activity is of the same order as values measured in mine waters from the lead mines of southeastern Missouri (Buckley, 1909).

The alternate case, results of which are shown in Column 2, has a dissolved carbonate activity close to that of rainwater in equilibrium with atmospheric CO₂. An analysis of the malachite precipitated, however, shows a CaO content of 1.5% (Table 1, number 7), indicating the presence of Ca⁺⁺ in the system. The initial assumptions (the presence of calcite) made, therefore, were probably more correct than the alternate case. It can be seen that under the conditions of Column 1, Table 7, CuCO₃° is the dominant copper ion (Figure 2, point C). Using free free energy data, the relationship between Cu⁺⁺ and CuCO₃° indicates 

\[ a(CuCO₃°) = 10^{-7.1} \]

in the system under consideration.

\[ Cu⁺⁺ + HCO₃⁻ = CuCO₃° + H^+ \]  

(15)

Paragenesis of Minerals

The paragenesis at the Silver Hill mine mentioned earlier was:

malachite-tenorite → malachite → rosasite.

The change from malachite-tenorite to malachite can be explained by an increase in copper or carbonate ion activity. There could be a number of explanations to explain the formation of rosasite after malachite.

1. One interpretation is that zinc was not introduced into the system until some time after the copper was introduced. If the minerals are formed as a result of oxidation of a vertically
zoned sulfide deposit, the uppermost zone is usually exposed to more intense leaching than the lower zone. In a mineral deposit consisting of narrow adjacent zones of copper and zinc, the leaching solutions should first contain both metal ions. As the leached zone moves downward, the upper zone of copper or zinc is entirely removed, and the solutions should contain only a single metal ion from the lower zone. The most likely case would be for the zinc to be below the copper so that the early solutions would have a high Cu:Zn ratio and the later solutions would have a much lower ratio as the copper is removed and the zinc is exposed to more intense leaching. The malachite at the Silver Hill mine was found to contain 0.4% ZnO (Table 1, sample 7).

2. The pH or carbonate ion activity in the system may have fluctuated such that the stability fields of the two minerals were progressively encountered. Free energy values are not available for rosasite, but a simple formula for the mineral with a Cu:Zn ratio of 1.5:1 can be written: \( \text{Cu}_6\text{Zn}_4(\text{OH})_{10}(\text{CO}_3)_5 \). Equilibrium of this compound with malachite could be expressed by

\[
\text{Cu}_6\text{Zn}_4(\text{OH})_{10}(\text{CO}_3)_5 + 6H^+ \rightleftharpoons 3\text{Cu}_2(\text{OH})_2\text{CO}_3 + 2\text{HCO}_3^- + 4\text{H}_2\text{O} + 4\text{Zn}^{2+}.
\]  

(16)

An increase in carbonate or zinc ion activity or pH should move equilibrium to the left. The increase in carbonate activity could conceivably be responsible for the change from malachite-tenorite to malachite as well as the change from malachite to rosasite.
3. Early leaching could have been under conditions of abundant water, and the soluble zinc ion might have been removed in solution. As the amount of water decreased, it became insufficient to remove the zinc which was then able to form a secondary mineral.

4. Zinc may have been introduced by a hydrothermal fluid which had already introduced the copper at an earlier time. This process is similar to the paragenesis of hydrothermal sulfides where zinc minerals sometimes form later than copper minerals. The paragenesis at the Silver Hill mine may be a repetition of the common copper–zinc sulfide sequence with the carbonate ion replacing the sulfide ion under oxidizing conditions.

Discussion of Results

The C\(^{14}\) determination with the malachite shows the mineral to be older than 41,000 years before present. The carbonate activity in water containing atmospheric CO\(_2\) reacting with limestone is much lower than that calculated for the system under consideration (compare Columns 1 and 3, Table 7). This excess carbonate in the system could come from leached carbonate rocks, ground water, or juvenile waters. If it comes from leached carbonate rocks, the pH of the leaching solution would necessarily be lower than that accounted for by atmospheric carbonic acid. This increase in acidity could be caused by humic acids or the acids formed by oxidation of sulfides.

The acid solution would release from limestone the carbonate which was incorporated into the malachite. The age of the C\(^{14}\) should
then reflect the age of the source for the carbonate instead of the age of the malachite. If the Horquilla limestone had been the source for the carbonate, this method would give the malachite a Pennsylvanian age, even though it may have formed more recently. This procedure, moreover, must be modified to take into account the contribution of CO₂ by decaying organic matter which accounts for a significant amount of the carbonate present in ground water (Damon, oral communication).

The C^{13} analysis indicates the malachite to be typical of either oxidation zone carbonates or metasomatic carbonates. Since the Silver Hill mine is in a metasomatic zone adjacent to the Silverbell porphyry, either origin indicated by C^{13} is compatible with field evidence.

Theoretical values determined for the composition of the solutions from which the malachite was deposited are similar to values measured in the field for waters in areas of oxidized sulfide ores in limestone. This agreement would support the C^{13} value for oxidation zone carbonates.

Conclusions

The history of the Silver Hill mine might be reconstructed as follows:

1. Early silicification and mineralization with sulfides. Although sulfides were not present in the system investigated, they are assumed to be the source of the Cu^{++}, Zn^{++}, and Pb^{++} present in the malachite which was analyzed.

2. Supergene fluids entering the system formed secondary kaolinite on fractures and were acidic enough in character to permit
kaolinite stability. If these solutions were basic, montmorillonite (or beidellite) would be stable and chrysocolla might have formed instead of malachite (Hemley, Meyer, and Richter, 1961).

3. Solutions became less acidic permitting the precipitation of leached Cu$^{++}$ as malachite in fractures.

4. One of two possibilities resulted in precipitation of rosasite:
   a. Close zoning of copper stratigraphically higher than zinc occurred so that early leaching solutions consisted primarily of copper. As time went on, these solutions became richer in both zinc and carbonate activity.
   b. Deposition of early malachite proceeded during a period of considerable rainfall sufficiently high to (1) prevent immobilization of malachite as a surface stain, (2) keep enough zinc in solution to prevent the formation of a mixed carbonate of copper and zinc, and (3) supply some lead to the system. The amount of rainfall then decreased, zinc was no longer retained in solution, and the formation of rosasite resulted.

If 4b is the case, as is more likely, deposition of early malachite occurred during a period of considerable rainfall, but this period of humid climate was probably not that of the recent pluvial period.

The genetic sequence and environment predicted by thermodynamics, carbon isotopes, and mineral relationships are consistent with those established for processes of oxidation and supergene deposition in an ore body which contained copper sulfide mineralization.
METHODS OF FORMATION OF PRIMARY MALACHITE

The formation of minerals such as malachite and chrysocolla is attributed to supergene oxidation of pre-existing copper sulfides. It is possible, however, that these minerals may form as a result of hypogene and mesogene processes as well. The primary requirement for such an occurrence would be conditions permitting the existence of the $+2$ copper ion. The sulfide activity should be low in order that the chalcophile affinity of copper does not result in the formation of covellite, which has been shown to be hypogene (Locke, Hall, and Short, 1924). The presence of a reactive anion such as carbonate or silicate could be obtained directly from the hydrothermal fluid or from ground water. Several methods of introduction of copper from depth are possible. Four of these which will be discussed separately are: (1) hydrothermal leakage from deeper deposits, (2) tenuous residual ore fluids, (3) near-surface intrusion related to volcanism, and (4) leaching of deep-seated mineralization by circulating ground waters.

Hydrothermal Leakage

The porphyry copper deposits of the southwestern United States are characterized in general by intrusion under moderate to low confining pressure. These intrusions frequently show evidence of being associated with local updoming which develops radial and concentric fracture patterns, breccia pipes, and stockworks.
Commonly associated with the main disseminated mineralization of the porphyries are sulfide-bearing quartz veins. These veins are thought to have formed from aqueous solutions which carried sulfides away from the main body of mineralization and deposited them in surrounding fractures. Since these veins form under essentially the same conditions as the disseminated sulfides, they contain the same type of mineral assemblage as the main body.

If such veins can form by hydrothermal leakage around and away from the main body of mineralization, the fluids might also move upward toward the surface along fractures. These ascending solutions might be expected to form an entirely different mineral assemblage than that formed by lateral leakage because the metal-bearing solutions would become oxidized as they approached the surface. If the ground-water table was encountered, minerals typical of the oxide zone might form by interaction with reactive anions. The source of the anions could be either from the hydrothermal fluid directly or from an external source such as ground water.

Residual Ore Fluids

Hydrothermal fluids from which copper sulfides have precipitated may contain sufficient copper to satisfy the solubility relations of the various copper sulfides under the prevailing conditions. As the sulfide activity decreases, the copper ion activity will increase unless sulfide complexes are formed. Residual fluids might contain sufficient copper to produce oxide zone minerals when the solutions reach the ground-water table by the processes discussed just above.
This process differs from direct hydrothermal precipitation in that it occurs after, rather than during, the precipitation of sulfides at depth. If the sulfide activity at depth was high, the copper activity in the residual ore fluid would be depressed to essentially insignificant amounts.

Near-surface Intrusion

Hydrothermal fluids associated with near-surface intrusions, and conceivably extrusions, would introduce metals into the region of normal formation of secondary minerals. The affinity of copper for mafic and intermediate rocks could account for the introduction of copper with volcanism. Zies (1929) found significant amounts of metals associated with fumarolic activity. Intrusions in the ground-water region would have a ready source for transporting fluids which may have been absent in the original magma.

Deep Circulating Ground Water

White (1955), in a discussion of thermal springs, concludes that the water in these springs is chiefly of meteoric origin. Lindgren (1933, p. 42), referring to circulation of ground water in deep-seated igneous rocks states:

The surface waters penetrating them [the igneous rocks] are charged with more or less carbon dioxide, which, at ordinary temperatures, gradually decomposes the silicates, particularly the pyroxene, amphibole, biotite and the calcium feldspars... the springs in such terranes have a low salinity, rarely above 1000 parts per million [due to the small amounts of soluble salts in the rocks] and will contain principally calcium carbonate... there will be little chlorine and sulphuric acid radical... the silica is relatively high... such calcium carbonate waters are characteristic of... deeper circulation in crystalline terranes... where they traverse mineral deposits, metals contained in the deposits will,
of course, be dissolved . . . where the rocks contain much pyrite . . . the sulfates . . . rapidly increase in the waters.

Solution of chalcopyrite is favored by high pH and Eh conditions as shown by

\[ \text{CuFeS}_2 + 10H_2O \rightarrow \]

\[ \text{HCUO}_2^- + \text{Fe}^{+3} + 2\text{SO}_4^{=} + 19\text{H}^+ + 17e^- \]  

(17)

The HCUO$_2^-$ complex was chosen for copper because of its stability at high pH values. Similarly, meteoric waters charged with carbon dioxide would also favor the solution of chalcopyrite by formation of the CuCO$_3^0$ complex as shown by

\[ \text{CuFeS}_2 + \text{CO}_2 + 9\text{H}_2\text{O} \rightarrow \]

\[ \text{CuCO}_3^0 + \text{Fe}^{+3} + 2\text{SO}_4^{=} + 18\text{H}^+ + 17e^- \]  

(18)

Exothermic oxidation reactions would heat up the leaching solutions causing them to move toward the surface in response to a thermal gradient. Mixing of these ascending solutions with groundwater could result in precipitation of metals by interaction with reactive anions or by destruction of complexes. As shown by Figure 8, waters containing copper at an activity of $10^{-4.0}$ and pH = 5 will not precipitate malachite (point A). However, dilution of the solution by a factor of 100 resulting in a drop in copper activity to $10^{-6.0}$ and pH to 7 (Figure 8, point B) will precipitate malachite. The carbonate activity was assumed to remain constant because, in the absence of carbonate rocks, the groundwater and leaching solutions contain only atmospheric CO$_2$.

Summary

Each of the models discussed suggests a means of introducing copper into the region of normal oxidation of sulfide deposits. The
Figure 8. Precipitation Curve for Malachite in the System Cu-H₂O-CO₂ at $\sum CO_2(aq) = 10^{-3.0}$
minerals which would form in such an environment would contain a cation introduced from depth and an anion introduced similarly or supplied by ground water. These two sources of anions would result in hypogene or mesogene minerals respectively and would differ from supergene minerals only in that the metal ion was introduced from depth. In the next chapter I shall discuss a mineral deposit which shows evidence of having formed in such a manner.
FIELD EVIDENCE OF HYPOGENE CHRYSOCOLLA

A group of vein deposits from southern California was studied using mineral equilibria and petrography. The investigation has revealed strong evidence of these deposits having formed from solutions which were not of supergene origin.

Field Relationships

A sketch map of the area is shown below:

Volcanics (volc) consisting of pyroclastic material and andesite flows form a broad band about 1/2 mile in width and 3 1/2 miles long trending about N. 80° E. The volcanics separate a complex of metamorphosed igneous and sedimentary rocks (mcx) to the south and a boulder conglomerate (qmc) which is closely related spatially and chronologically to the volcanics. Rough bedding in the conglomerate strikes N. 45° E. and dips 60° NW. To the north and west the area is covered by several square miles of alluvium (Qal).
The southern or lower portion of the conglomerate is made up of boulders of unaltered quartz monzonite and similar fine-grained material as matrix. No quartz monzonite was found to outcrop in the area so it is inferred that the source area for the conglomerate is covered by alluvium to the north or west. This inference is based partially on the fact that tilting from the southeast may account for the northwest dip of the conglomerate. The boulders of quartz monzonite are up to six feet in diameter which indicates relatively short or local transport. Moving upward stratigraphically from the base, the conglomerate contains a mixture of quartz monzonitic and volcanic material. The extreme northwest portion of the conglomerate is made up completely of volcanic material.

Cutting the lower half of the conglomerate are numerous andesite dikes and sills generally less than four feet across. These intrusions contain fragments of conglomerate material which show essentially no evidence of reaction with the andesite other than occasional chlorite rims less than 0.5 cm in width. Associated with the andesite (at D on the map) are small veinlets and coatings of chrysocolla, hematite, and calcite. These minerals are found on wallrocks around the intrusions and on fragments contained in the andesite.

Mineralization

The mineralization in the area consists of veins which cut the metamorphic complex (E on sketch map), volcanics (B and C), and the conglomerate (A and D). These veins show a weak northerly trend, striking from N. 45° E. to N. 45° W. and dipping steeply from 60° east to 60° west. Vein material consists of calcite, hematite, chrysocolla,
barite, and quartz. Three of the vein assemblages are shown in Figures 9, 10, and 11.

Calcite is dark brown to black and is coarsely crystalline and commonly makes up the majority of the vein-filling material. Hematite is brown and occurs as irregular masses and veinlets in most instances, but in the absence of calcite it may be the major vein mineral. Quartz is the α-variety and occurs late, filling open spaces with comb structures and veining the earlier minerals. Barite occurs later than calcite, hematite, and chrysocolla in most instances, but one vein of barite and chrysocolla shows the chrysocolla to have formed around plates of barite. Based on textural evidence, the genetic sequence appears to be:

Malachite is found in many veins closely associated with chrysocolla but does not occur in the absence of the copper silicate. This relationship and the abundance of calcite in the veins are strongly indicative of chrysocolla altering to malachite, but no definite evidence was found to indicate whether the malachite was associated with vein filling or later supergene processes.
Figure 9. Calcite Vein with Chrysocolla, Hematite, Barite, and Quartz (calcite, black; chrysocolla, blue; hematite, brown; barite and quartz, white).

Figure 10. Veins of Hematite and Chrysocolla.
Figure 11. Hematite Vein with Chryso-colla and Barite.
Discussion of Mineralization

Using the mineral assemblage present, the composition of the solution from which the minerals precipitated was calculated. The process used was similar to that used earlier for the Silver Hill mine and is shown in Appendix IV. The calculated composition appears in Table 8.

TABLE 8.--Calculated composition of solution in equilibrium with barite, calcite, chrysocolla, malachite, hematite, and quartz at pH = 8.4

<table>
<thead>
<tr>
<th>ion</th>
<th>log activity</th>
<th>ion</th>
<th>log activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4$$^-$</td>
<td>-2.7</td>
<td>H$^+$</td>
<td>-8.4</td>
</tr>
<tr>
<td>H$_2$CO$_3$$^0$</td>
<td>-5.0</td>
<td>Ca$^{++}$</td>
<td>-3.4</td>
</tr>
<tr>
<td>HCO$_3$$^-$</td>
<td>-3.0</td>
<td>Ba$^{++}$</td>
<td>-6.2</td>
</tr>
<tr>
<td>CO$_3$$^-$</td>
<td>-4.9</td>
<td>Cu$^{++}$</td>
<td>-23.4</td>
</tr>
<tr>
<td>H$_4$SiO$_4$$^0$</td>
<td>-4.0</td>
<td>Fe$^{+++}$</td>
<td>-25.9</td>
</tr>
</tbody>
</table>

If these minerals formed as a result of supergene processes, the source must have either been completely removed by erosion or is now buried under alluvium to the north and west because no evidence of earlier sulfides which could have served as a source of copper for chrysocolla was found in the area. The only sulfide found was covellite filling two veinlets less than 1 mm in width in the wallrock of one of the veins containing the chrysocolla-hematite-barite assemblage. The covellite appears to be very early and may be a result of early precipitation of small amounts of sulfide present in the solution by copper due to its chalcophile affinity. Covellite also indicates that the sulfide did form under oxidizing conditions. The presence of barite in veins is
strong evidence that the veins formed as a result of hypogene hydrothermal processes.

The calculated composition of the solution from which the vein minerals formed is compatible with a ground-water origin for the solution. The pH determined is reasonable for a ground-water environment in which no oxidizing sulfides were present to develop a strongly acid pH in the absence of limestone. The low activity of copper and iron permitted by the system indicates that if these ions were introduced they would precipitate immediately as chrysocolla and hematite respectively.

Based on field observation, mineralization appears to be related to the near-surface volcanism in the area. The andesite dikes may have introduced the mineralizing solutions, but it is more likely that the solutions which formed the veins are of ground-water origin and the intrusions served as a source of copper and possibly iron. The volcanism may also have introduced the carbonate which is so abundant in the veins.

Summary

The veins in the area studied consist, with the exception of barite, of a mineral assemblage typical of the zone of supergene oxidation of copper-iron sulfide mineralization. The anomalous presence of barite, which is commonly associated with hypogene processes, indicates that the veins may be of hydrothermal origin. If such was the case, the veins are probably related to near-surface andesite intrusions. A hypogene origin is further suggested by the lack of evidence of pre-existing sulfides in the area.
SUMMARY AND CONCLUSIONS

A detailed investigation of malachite and related minerals has revealed answers to some questions involving their formation and alteration. Chemical thermodynamics has been a major factor in explaining the properties and behavior of these minerals. Free energy values at 25°C and one atmosphere total pressure are sufficient for most investigations of the type considered because the minerals generally form at or near the earth's surface.

Copper carbonate complexes play an important part in formation and alteration of malachite, azurite, and tenorite. These complexes may also play a significant role in transport of metals in hydrothermal solutions. The solubility of the Cu$^{+2}$ ion is increased significantly by formation of complexes at normal ground-water carbonate activities. Dilution of solutions containing such complexes results in destruction of the complexes, and this may be significant in formation of mesogene minerals.

Azurite was shown to decompose at a low temperature in aqueous solutions but is stable at much higher temperatures under dry conditions. Malachite is stable in aqueous solutions up to the boiling point of water. Under dry conditions it decomposes at a slightly lower temperature than azurite.

Differential thermal analysis of malachite accompanied by infrared analysis of products indicates that this mineral decomposes by first losing adsorbed water followed by loss of structural water. This results
in the compound CuCO$_3$ which had not been previously recognized. Further heating results in loss of CO$_2$. The temperature at which dry decomposition of malachite and azurite begins indicates that these minerals may be stable under mesothermal conditions if no water is present.

Study of a vein occurrence of malachite with thermodynamics and mineral stabilities has revealed an environment of increasing pH and carbonate activity with time. Such a process is compatible with oxidation of sulfides in a limestone environment followed by neutralization and redeposition of copper from leaching solutions. The C$^{12}$/C$^{13}$ ratio in the malachite is similar to values obtained from oxidation zone carbonates. C$^{14}$ age-dating of the malachite indicates that it did not form during the recent pluvial period in Arizona.

An investigation of a chrysocolla vein deposit showed that strong evidence can be presented in favor of the formation of this mineral as a mesogene or hypogene mineral related to volcanism. The formation of chrysocolla and other such minerals under hydrothermal conditions indicates that many of the previously accepted ideas concerning "secondary" minerals may warrant reinvestigation.
APPENDIX I

INFRARED ANALYSIS OF MALACHITE AND OTHER SELECTED MINERALS

Infrared spectroscopy is a method of investigating the vibrational activation of molecules. It is based on the principle of absorption of incident radiation by a molecule when the frequency of this radiation is very near the natural frequency of a bond within the molecule. Bond lengths in any molecule will depend on the structure of the entire molecule. Certain functional groups within the molecule, however, will give characteristic absorption frequencies, and the same group should have about the same characteristic frequencies in other molecules.

Infrared spectra are complex, and as a result, it is highly improbable that two different compounds will have identical spectra. The complexity of spectra is proportional to the number of different bonds in a molecule; for instance, the complexity increases from oxides to basic oxides (Figure 12, a and b) and from carbonates to basic carbonates (Figure 12, c and d).

Samples were powdered and dispersed in 325 mg of KBr. KBr is used as a carrier because it shows no absorption in the spectral range 400 to 47,500 cm\(^{-1}\). The sample in KBr is then held under 20,000 pounds pressure for three minutes to form a clear disc one centimeter in diameter. The concentration of the sample must be on the order of 1% in KBr by weight. Higher concentrations tend to cloud the pellet, and lower
Figure 12. Infrared Spectra of Selected Minerals

(A) $\text{Fe}_2\text{O}_3$ hematite
(B) $\text{HFeO}_2$ goethite
(C) $\text{ZnCO}_3$ smithsonite
(D) $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ hydrozincite
(E) CuO tenorite
(F) ZnO zincite
concentrations are not detected. Samples of various oxides, carbonates, and basic carbonates were scanned with a Beckman IR-10 from 300 to 4,000 cm$^{-1}$.

As a result of investigations, certain similarities were found between the same types of compounds:

1. Oxides of Cu, Zn, and Fe show transmission in the region 600–800 cm$^{-1}$ (Figure 12, a, e, and f).

2. Carbonates of Ca, Fe, Zn, and Pb have similar absorption spectra. Calcite, siderite, and smithsonite are hexagonal rhombohedral carbonates, and each has a broad peak at 1410 cm$^{-1}$ and a small peak at about 1800 cm$^{-1}$ (Figure 13, a, b, and c). Cerussite, an orthorhombic carbonate, has the broad peak at 1385 cm$^{-1}$ and the small peak at 1720 cm$^{-1}$ (Figure 13, d). All of the carbonates have a group of sharp characteristic peaks below 1050 cm$^{-1}$. A compound tentatively identified as CuCO$_3$ has a broad peak at 1385 cm$^{-1}$ (Figure 13, e) which is similar to orthorhombic carbonates.

3. Basic carbonates of Zn, Cu, Mg, and Zn–Cu have two characteristic peaks, one at 1350–1410 cm$^{-1}$ and another at 1470–1550 cm$^{-1}$ corresponding to the CO$_3^{2-}$ and OH$^-$ functional group. All have a complex group of peaks in the region 700–1200 cm$^{-1}$ (Figure 14).

Ideally, the height of any given peak is proportional to the concentration of the bond responsible for the peak. The peak may be affected, however, by impurities, crystal defects, isomorphous
Figure 13. Infrared Spectra of Carbonates

- CaCO_3 (calcite)
- FeCO_3 (siderite)
- ZnCO_3 (smithsonite)
- PbCO_3 (cerussite)
- CuCO_3 (?) DTA
Figure 14. Infrared Spectra of Basic Carbonates

- **hydrozincite** \( \text{Zn}_5(\text{OH})_6(\text{CO}_3)_2 \)
- **hydromagnesite** \( \text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O} \)
- **malachite** \( \text{Cu}_2(\text{OH})_2\text{CO}_3 \)
- **azurite** \( \text{Cu}_3(\text{OH})_2(\text{CO}_3)_2 \)
- **rosasite** \( (\text{Cu},\text{Zn})_2(\text{OH})_2\text{CO}_3 \)
substitutions, and other factors which modify the electron structure of the compound.

Eleven peaks were selected for the malachite samples, and the peak heights measured for each of the eleven samples. The peak heights of all samples were then standardized to the 1380 cm\(^{-1}\) peak of sample J, in order to compensate for the different amounts of malachite in each pellet. The 1380 cm\(^{-1}\) peak was chosen because the CO\(_3^{2-}\) concentration in malachite is more likely to be constant than the OH\(^-\) concentration due to adsorbed water. Sample A, however, was standardized to the 700 cm\(^{-1}\) peak, the height of which was common to a majority of the samples. This was done because the mode of origin of Sample A could permit the presence of excess carbonate from oxidized organic material. The spectra are shown in Figure 15, and the peak heights are presented in Table 9.
Figure 15. Infrared Spectra of Various Malachite Samples
TABLE 9.—Infrared peak heights of malachite samples standardized to 1380 cm⁻¹ peak of sample J

<table>
<thead>
<tr>
<th>peak cm⁻¹</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
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<td>1495</td>
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<td>51.5</td>
<td>49.0</td>
<td>50.5</td>
<td>49.0</td>
<td>48.5</td>
<td>50.5</td>
<td>49.0</td>
<td>47.0</td>
</tr>
<tr>
<td>1430</td>
<td>43.5</td>
<td>49.0</td>
<td>45.5</td>
<td>47.5</td>
<td>49.5</td>
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<td>54.0</td>
<td>54.0</td>
<td>54.0</td>
<td>54.0</td>
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<td>25.5</td>
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<td>20.0</td>
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</tr>
<tr>
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<td>50.5</td>
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<td>49.5</td>
<td>41.5</td>
<td>44.0</td>
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<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
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<td>49.5</td>
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<td>39.0</td>
<td>31.5</td>
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<td>29.0</td>
<td>31.5</td>
<td>39.5</td>
</tr>
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<td>26.0</td>
<td>26.0</td>
<td>26.0</td>
<td>26.0</td>
<td>32.0</td>
</tr>
</tbody>
</table>
APPENDIX II

$^{14}C$ AGE DETERMINATION OF MALACHITE

A sample of malachite from the Silver Hill mine was taken from the core of a large mass of malachite to avoid surface contamination by $^{14}C$ in recent meteoric waters. After grinding the sample to 100 mesh fineness, it was digested in 1N HCl. The volume of CO$_2$ obtained was only 50% of the volume which would be obtained with 100% recovery of carbon from the sample. This loss may have been due to retention of some CO$_3^-$ in solution as a complex with copper.

The $^{14}C$ activity of the CO$_2$ was measured in a 5-liter proportional counter. Calculations for determination of the age of the malachite are as follows:

- total counting time (min) = 2,340
- total count = 28,246
- total activity (counts/min) = 12.07±0.07
- background activity (counts/min) = 12.17±0.07
- net activity (counts/min) = 0.10±0.10

In order for the sample activity to be compared to a modern reference, the volumes of both samples measured should contain an equal number of moles of CO$_2$. Using the ideal gas law

\[ PV = nRT, \]

the volume (V) and the gas constant (R) are constant. The differences in pressure (P) and temperature (T), however, will determine the number of
moles of gas (n) present. Therefore,

\[ \frac{R}{V} = \text{constant} \]

\[ \frac{P(\text{ref})}{n(\text{ref}) \times T(\text{ref})} = \frac{P(\text{samp})}{n(\text{samp}) \times T(\text{samp})} \]

- \( P(\text{ref}) \) (mm Hg) = 700
- \( P(\text{samp}) \) (mm Hg) = 627
- \( T(\text{ref}) \) (°K) = 298
- \( T(\text{samp}) \) (°K) = 295.7

\( n(\text{samp}) = 0.9 \times n(\text{ref}) = c \)

The age of the sample (t) is given by

\[ t = \frac{T_{1/2}}{0.693} \ln \left( \frac{c(s)}{x} \right) \]

where \( s \) and \( x \) are the modern standard count and sample count respectively, \( T_{1/2} \) is the half-life of \( ^{14} \text{C} \) (5,730 yrs), \( c \) is the ratio of moles of sample to moles of reference. Modern sample count determined with N.B.S. oxalic acid is 30.70±0.25. The sample count is essentially zero, and using the 2σ criteria

\[ t > \frac{5730}{0.693} \ln \left( \frac{30.70}{0.20} \right) \]

\[ > 41,000 \text{ years before present.} \]
APPENDIX III

CALCULATION OF COMPOSITION OF SOLUTION
DEPOSITING MALACHITE AT SILVER HILL MINE

The free energy change ($\Delta F$) of a reaction is the sum of the free energies of the products minus the sum of the free energies of the reactants.

$$\Delta F(\text{reaction}) = \Delta F(\text{products}) - \Delta F(\text{reactants})$$

The free energy change is related to activities ($a$) of products and reactants by the equation:

$$\Delta F = -1.364 \log \frac{(a_B)^b(a_C)^c}{(a_D)^d(a_E)^e}$$

for the equation:

$$bB + cC \rightleftharpoons dD + eE$$

Gas fugacities may be substituted for ionic activities in either of these equations. Since the log function in the above reaction is equal to the equilibrium product ($K_{eq}$) of the reaction, the equilibrium product of a reaction can be calculated by the equation:

$$K_{eq} = \log \frac{(a_B)^b(a_C)^c}{(a_D)^d(a_E)^e} = \frac{\Delta F}{-1.364}$$

Free energy values used for calculations in the text and in this section are listed in Appendix V.

The necessary equations to calculate the results found in Table 4 and their associated activity products are as follows:
\[
\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3
\]
\[
a(\text{H}_2\text{CO}_3) = 10^{-1.5} \times P(\text{CO}_2) \tag{19}
\]

\[
\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-
\]
\[
a(\text{HCO}_3^-) = \frac{a(\text{H}_2\text{CO}_3) \times 10^{-6.4}}{a(\text{H}^+)} \tag{20}
\]

\[
\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^-
\]
\[
a(\text{CO}_3^-) = \frac{a(\text{HCO}_3^-) \times 10^{-10.3}}{a(\text{H}^+)} \tag{21}
\]

\[
\text{CaCO}_3 = \text{Ca}^{++} + \text{CO}_3^-
\]
\[
a(\text{Ca}^{++}) = \frac{a(\text{CO}_3^-) \times 10^{-8.3}}{a(\text{CaCO}_3)} \tag{22}
\]

\[
\text{Cu}_2(\text{OH})_2\text{CO}_3 = 2\text{Cu}^{++} + 2\text{OH}^- + \text{CO}_3^-
\]
\[
a(\text{Cu}^{++})^2 = \frac{a(\text{Cu}_2(\text{OH})_2\text{CO}_3) \times 10^{-33.7}}{a(\text{OH}^-)^2 \times a(\text{CO}_3^-)} \tag{23}
\]

\[
\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-
\]
\[
a(\text{OH}^-) = \frac{10^{-14}}{a(\text{H}^+)} \tag{24}
\]

The activity of an ion in solution \((a_M)\) is equal to the product of the
molality of the ion \((m_M)\) and the activity coefficient of the ion \((\gamma_M)\).
\[
a_M = m_M \times \gamma_M \tag{25}
\]

The activity coefficient of each ion is determined by the Debye Hückel
equation
\[
-\log \gamma_M = \frac{A z_M^2 \sqrt{I}}{1 + a_O^O \sqrt{I}}
\]
where \( A \) and \( B \) are constants for various temperatures (equal to 0.5085 and 0.3281 respectively at 25°C), \( z_M \) is the ionic charge of ionic species \( M \), and \( a^o \) is a value which is related to the "specific diameter" of the ion in solution. Values of \( a^o \) for the ions under consideration are (Garrels and Christ, 1965):

<table>
<thead>
<tr>
<th>ion</th>
<th>( a^o )</th>
<th>(-\log\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ )</td>
<td>9x10^{-8}</td>
<td>-0.024</td>
</tr>
<tr>
<td>( \text{OH}^- )</td>
<td>3.5x10^{-8}</td>
<td>-0.027</td>
</tr>
<tr>
<td>( \text{Ca}^{++} )</td>
<td>6x10^{-8}</td>
<td>-0.101</td>
</tr>
<tr>
<td>( \text{CO}_3^{=} )</td>
<td>4.5x10^{-8}</td>
<td>-0.100</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>4.0x10^{-8}</td>
<td>-0.026</td>
</tr>
<tr>
<td>( \text{Cu}^{++} )</td>
<td>6x10^{-8}</td>
<td>-0.101</td>
</tr>
</tbody>
</table>

The total ionic strength (I) is given by

\[
I = \frac{1}{2} \sum m_M (z_M)^2.
\]

Assuming a total ionic strength of 0.003 for a dilute solution (Garrels and Christ, op. cit.), the activity coefficients for the various ions can be calculated and are found in the table above with the \( a^o \) values.

Equations 20, 21, 22, 23, and 24 can then be rewritten as Equations 26, 28, 30, 32, and 34 respectively.

\[
m(\text{HCO}_3^-) = \frac{10^{-6.4} \times m(\text{H}_2\text{CO}_3)}{m(\text{H}^+) \times \gamma(\text{H}^+) \times \gamma(\text{HCO}_3^-)}
\]

\[
= \frac{10^{-6.4} \times m(\text{H}_2\text{CO}_3)}{m(\text{H}^+) \times 10^{0.0} \times 10^{0.0}}
\]

\[
= \frac{10^{-6.4} \times m(\text{H}_2\text{CO}_3)}{m(\text{H}^+)}
\]
\[ m(CO_3^{-}) = \frac{10^{-10.3} \times m(HCO_3^-) \times \gamma(HCO_3^-)}{m(H^+) \times \gamma(H^+) \times \gamma(CO_3^-)} \]  
\[ = \frac{10^{-10.3} \times m(HCO_3^-) \times 10^{0.0}}{m(H^+) \times 10^{0.0} \times 10^{0.1}} \]  
\[ = \frac{10^{-10.4} \times 10^{-6.4} \times m(H_2CO_3)}{m(H^+) \times m(H^+)} \]  
\[ = \frac{10^{-16.8} \times m(H_2CO_3)}{m(H^+)^2} \]  
\[ m(Ca^{++}) = \frac{10^{-8.3}}{m(CO_3^{-}) \times \gamma(CO_3^{-}) \times \gamma(Ca^{++})} \]  
\[ = \frac{10^{-8.3}}{m(CO_3^{-}) \times 10^{0.1} \times 10^{0.1}} \]  
\[ = \frac{10^{-8.5} \times m(H^+)^2}{10^{-16.8} \times m(H_2CO_3)} \]  
\[ m(Cu^{++}) = \left[ \frac{10^{-33.7}}{m(OH^-)^2 \times \gamma(OH^-)^2 \times m(CO_3^{-}) \times \gamma(CO_3^-)} \right]^{1/2} \]  
\[ = \left[ \frac{10^{-33.7}}{m(OH^-)^2 \times (10^{0.1})^2 \times m(CO_3^{-}) \times 10^{0.1}} \right]^{1/2} \]  
\[ = \left[ \frac{10^{-34.0} \times m(H^+)^2 \times m(H^+)^2}{10^{-28.0} \times 10^{-16.8} \times m(H_2CO_3)} \right]^{1/2} \]  
\[ = \left[ \frac{10^{-10.8} \times m(H^+)^4}{m(H_2CO_3)} \right]^{1/2} \]
Since the value of \( P(\text{CO}_2) \) is defined by the system being on a phase boundary (Figure 3), Equation 19 can be used to determine the molal concentration of \( \text{H}_2\text{CO}_3 \):

\[
m(\text{H}_2\text{CO}_3) = 10^{-1.5} \cdot P(\text{CO}_2)
\]

\[= 10^{-1.5} \cdot 10^{-3.8}
\]

\[= 10^{-5.3}.
\]

Equations 26, 28, 30, and 32 can be used to evaluate the molality of each ion in terms of \( m(\text{H}^+) \). The values for the various ions are:

\[m(\text{HCO}_3^-) = \frac{10^{-11.7}}{m(\text{H}^+)}\]

(37)

\[m(\text{CO}_3^{2-}) = \frac{10^{-22.3}}{m(\text{H}^+)^2}\]

(38)

\[m(\text{Ca}^{++}) = 10^{13.6} \times m(\text{H}^+)^2\]

(39)

\[m(\text{Cu}^{++}) = 10^8.1 \times m(\text{H}^+)^2\]

(40)

Assuming that the ions considered are the only ones present in significant amounts to affect the ionic strength, the following equation must be satisfied in order to maintain electrical neutrality:

\[
\sum m_M \times z^+ = \sum m_M \times z^-
\]

(41)
Substituting the appropriate ions gives:

\[ 2m(\text{Cu}^{2+}) + 2m(\text{Ca}^{2+}) + m(\text{H}^+) = m(\text{OH}^-) + m(\text{HCO}_3^-) + 2m(\text{CO}_3^{2-}) \]

\[ 2 \times 10^{8.1}m(\text{H}^+)^2 + 2 \times 10^{13.6}m(\text{H}^+) + m(\text{H}^+) = \]

\[ \frac{10^{-14.0}}{m(\text{H}^+)} + \frac{10^{-11.7}}{m(\text{H}^+)} + 2 \times \frac{10^{-22.3}}{m(\text{H}^+)^2} \]

\[ 10^{13.9}m(\text{H}^+)^4 + 10^{8.4}m(\text{H}^+)^4 + m(\text{H}^+)^3 = \]

\[ 10^{-14.0}m(\text{H}^+) + 10^{11.7}m(\text{H}^+) + 10^{-22.0} \]

\[ (10^{13.9} + 10^{8.4}m(\text{H}^+)^4 + m(\text{H}^+)^3 - (10^{-14.0} + 10^{-11.7})m(\text{H}^+) = \]

\[ 10^{-22.0}. \]

Solving by trial and error,

\[ m(\text{H}^+) = 10^{-8.5}. \]

The molalities of the various ions are calculated by substitution of the values of \( m(\text{H}^+) \) and \( m(\text{H}_2\text{CO}_3) \) into Equations 35, 37, 38, 39, and 40. Activities of the ions are then calculated using Equation 25. The resulting values are given in Table 7, Column 1 in the text.
APPENDIX IV

CALCULATION OF COMPOSITION OF POSSIBLE HYDROTHERMAL SOLUTION WHICH PRECIPITATED CHRYSOCOLLA

The mineral assemblage consisting of barite, calcite, chrysocolla, hematite, and quartz can be used to approximate the composition of the aqueous solution with which these minerals are in equilibrium. Since the deposit shows evidence of having formed close to the surface, STP conditions can be assumed.

Reactions can be written which place limits on the fugacities of O$_2$, S$_2$, and CO$_2$ in the system. These reactions are then plotted on a trivarient diagram with O$_2$, S$_2$, and CO$_2$ fugacities as variables. Chrysocolla, however, cannot be plotted simply as a function of these three gases because it forms from the aqueous silica ion by the reaction:

$$\text{CuSiO}_3 \cdot \text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + \text{H}_4\text{SiO}_4^0.$$  \hspace{1cm} (42)

The formula used here for chrysocolla ($\text{CuSiO}_3 \cdot \text{H}_2\text{O}$) represents an idealized composition which was used by Newberg (1967) to obtain free energy data for the mineral.

An approximation of the concentration of silica ion in the solution can be made using the dissociation of quartz:

$$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4^0.$$  \hspace{1cm} (43)

The resulting $\text{H}_4\text{SiO}_4^0$ complex dissociates by the reaction

$$\text{H}_4\text{SiO}_4^0 \rightarrow \text{H}^+ + \text{H}_3\text{SiO}_4^-.$$  \hspace{1cm} (44)

Equilibrium for Equation 44 occurs at pH = 9.9, and at pH values below
about 9.0 the dominant silica species in solution is $H_4SiO_4^\circ$. The $H_4SiO_4^\circ$ activity determined by Equation 43 is $10^{-4.0}$. Using this approximation, reactions defining chrysocolla stability can then be written.

Several mineral pairs can be used to place boundaries on the composition of the solution precipitating barite, calcite, chrysocolla, hematite, and quartz. In each of the reactions written below, the stable mineral is written as the reaction product.

1. Witherite $\rightarrow$ barite
   $$2BaCO_3 + S_2 + 3O_2 \rightarrow 2BaSO_4 + 2CO_2$$ (45)

2. Anhydrite $\rightarrow$ calcite
   $$2CaSO_4 + 2CO_2 \rightarrow 2CaCO_3 + S_2 + 3O_2$$ (46)

3. Pyrite $\rightarrow$ hematite
   $$4FeS_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4S_2$$ (47)

4. Malachite $\rightarrow$ chrysocolla
   $$Cu_2(OH)_2CO_3 + 2H_4SiO_4^\circ \rightarrow 2CuSiO_3 \cdot H_2O + CO_2 + 3H_2O$$ (48)

5. Brochantite $\rightarrow$ chrysocolla
   $$2Cu_4(OH)_6SO_4 + 8H_4SiO_4^\circ \rightarrow 8CuSiO_3 \cdot H_2O + S_2 + 3O_2 + 14H_2O$$ (49)

6. Magnetite $\rightarrow$ hematite
   $$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$$ (50)

Each of these reactions is plotted on Figure 16 as a function of $S_2$, $O_2$, and $CO_2$ fugacities at $a(H_4SiO_4^\circ) = 10^{-4.0}$. 
Figure 16. Stability Boundaries of Mineral Pairs

Darkened area shows boundaries on stability of ba, cal, hm, and xy.
The darkened areas on Figure 16 show composition boundaries on the solution precipitating the mineral assemblage under consideration. The chrysocolla-malachite boundary places an upper limit of \( f(\text{CO}_2) = 10^{-9.9} \) on the solutions. These veins, however, appear to have formed close enough to the surface to suggest that the solution should have been in equilibrium with atmospheric \( \text{CO}_2 \) (\( f = 10^{-3.5} \)). If this is true, the malachite seen with the veins may have formed with the vein minerals rather than as a secondary alteration product of chrysocolla.

A large number of combinations of \( f(\text{CO}_2) \), \( f(\text{S}_2) \), and \( f(\text{O}_2) \) can be selected which lie within the mutual stability region of the minerals. A value of \( f(\text{CO}_2) = 10^{-3.5} \) has been selected based on the assumption of equilibrium between the solution and atmospheric \( \text{CO}_2 \) because no carbonate rocks were found in the area. The values chosen for \( f(\text{O}_2) \) and \( f(\text{S}_2) \) must be sufficient to form enough sulfate ion to give reasonable values for barium ion activity in the solution in equilibrium with barite.

I have assumed what I consider to be reasonable values for \( f(\text{CO}_2) \), \( f(\text{S}_2) \), and \( f(\text{O}_2) \) in aqueous solution in a near-surface environment. These are

\[
\begin{align*}
f(\text{CO}_2) &= 10^{-3.5} \\
f(\text{O}_2) &= 10^{-10} \\
f(\text{S}_2) &= 10^{-200}.
\end{align*}
\]

The sulfuric acid activity is established using the reaction

\[
\text{S}_2 + 2\text{H}_2\text{O} + 3\text{O}_2 \rightleftharpoons 2\text{H}_2\text{SO}_4^0
\]

\[
(\text{H}_2\text{SO}_4) = 10^{-19.5}.
\]
This value is then used to write the sulfate ion activity as a function of hydrogen ion activity with the reaction

$$\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}. \quad (52)$$

By a process similar to that used in Appendix III, the activity of each of the ions in the solution is written as a function of hydrogen ion activity. In order to satisfy electrical neutrality, the following relation must be satisfied

$$m(\text{H}^+) + 2m(\text{Cu}^{++}) + 2m(\text{Ca}^{++}) + 2m(\text{Ba}^{++}) + 3m(\text{Fe}^{+++}) =
$$

$$m(\text{OH}^-) + m(\text{HCO}^-) + 2m(\text{CO}_3^{2-}) + 2m(\text{SO}_4^{2-}).$$

Molalities for the various ions can be substituted for their activities because, as was demonstrated in Appendix III, there is little difference between these functions in a dilute solution.

The hydrogen ion activity determined by the electrical neutrality equation ($10^{-8.4}$) is used to calculate molalities of each of the ions in solution. The results of these calculations are shown in Table 8 in the text.
### APPENDIX V

FREE ENERGY VALUES AT 25°C USED FOR EQUILIBRIUM CALCULATIONS IN TEXT

<table>
<thead>
<tr>
<th>species</th>
<th>state</th>
<th>mineral</th>
<th>F (kcal/mole)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba⁺⁺</td>
<td>aqueous</td>
<td>-</td>
<td>-134.0</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>solid</td>
<td>witherite</td>
<td>-272.2</td>
</tr>
<tr>
<td>BaSO₄</td>
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</tr>
<tr>
<td>Ca⁺⁺</td>
<td>aqueous</td>
<td>-</td>
<td>-132.2</td>
</tr>
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<td>calcite</td>
<td>-269.8</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>solid</td>
<td>anhydrite</td>
<td>-315.6</td>
</tr>
<tr>
<td>CO₂</td>
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*From Garrels and Christ (1965) except where noted.*
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**Value calculated for initial precipitation of amorphous copper silicate from aqueous solution (Newberg, 1967).**
REFERENCES


Damon, P. E., Personal communication: Dept. of Geology, University of Arizona.


