Some Notes on the Composition of "Copper Pitch"

Richard R. Matthew

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SOME NOTES ON THE COMPOSITION OF  
"COPPER PITCH"

by

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Butte, Montana

MONTANA SCHOOL OF MINES  
Butte, Montana  
June 3, 1932
SOME NOTES ON THE COMPOSITION OF "COPPER PITCH"

Inaugural Thesis
submitted
As a partial fulfillment of the requirements
for the degree of

BACHELOR OF SCIENCE
in
Geological Engineering
from the
Montana School of Mines

8846

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By

RICHARD R. MATTHEW,
Butte, Montana

MONTANA SCHOOL OF MINES
Butte, Montana
June 3, 1932
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SOME NOTES ON THE COMPOSITION OF
"COPPER PITCH"

by

RICHARD R. MATTHEW

INTRODUCTION

A supply of so-called "copper pitch" ore was received by the Montana Bureau of Mines and Geology in response to a request by them from a resident of Kalispell, who had previously sent a specimen to the Bureau for a mineralogical analysis.

Since this material was little known and had apparently received but little study under a reflecting microscope\(^1\), it was thought that such a study might throw some light on the mineralogical and chemical composition of the material.

The results of this study are herein offered as partial fulfillment of the requirements for a Bachelor of Science Degree in Geology from the Montana School of Mines.

PREVIOUS WORK

"Copper pitch" is found in a number of oxidized copper veins. It has been found in larger quantities

\(^1\) Short, M. M. Microscopic Determination of the Ore Minerals, U. S. G. S. Bull. 825, pp. 82.
at and near Bisbee, Arizona, than elsewhere, but it has also been found in a great number of copper veins in Idaho\(^{(1)}\), at Butte, Montana, (personal observation) and near Kalispell, Montana.

It is a pitchy lustrous to dull black material with a hardness of from 3 to 4 and a specific gravity of from 4 to 4.5.

Examinations of this material have been made by Dr. G. A. Koenig\(^{(2)}\) in 1902, and by Hunt and Kraus in 1916\(^{(3)}\). Also, as mentioned before, M. N. Short has apparently examined polished sections of the material, for in "Microscopic Determination of the Ore Minerals" Bulletin 825 of the United States Geological Survey, he refers to tenorite under copper pitch and there states that tenorite with over 5% manganese oxide or silica is known as "copper pitch". In view of the fact that neither Koenig or Hunt report manganese in the copper pitch analysed by them and secondly in view of the fact that the material examined by the writer from Kalispell and from Bisbee contained only traces of manganese, it would seem that Mr. Short's statement was somewhat erroneous. The results of the present


study show that manganese or silica are not the most important impurities in tenorite which give it the name "copper pitch".

Dr. Koenig carefully examined a specimen of "copper pitch" from Bisbee and made an exact chemical analysis of it. As his examination of the material lead him to believe that it was homogenous, he calculated the formula \( \text{Cu}_2(\text{Si C})_2 \cdot \text{Cu(OH)}_2 \) for it and proposed that it be called melanochalcite.

Later Hunt and Kraus examined some material from the same general locality and Hunt made an analysis. This analysis was not in agreement with Koenig's, so Hunt and Kraus came to the conclusion that the material was a mixture. Additional evidence for this was found on examining some of the powdered material under a microscope. They found that three different kind of particles were present and distinguishable under polarized light. One kind of particle was dark and opaque, the other two were doubly refractive, one giving normal extinction and another not showing extinction at all, but giving anamalous colors under polarized light. They found that the doubly refractive material, which showed normal extinction, effervesced in HCl, so concluded that it was malachite. They then recalculated Koenig's analysis and calculated Hunt's on the assumption that
the material was a mixture of tenorite, malachite, and chrysocolla. These calculations are shown as follows:

**Koenig's Analysis**

<table>
<thead>
<tr>
<th>Molecular ratios</th>
<th>Malachite</th>
<th>Chrysocolla</th>
<th>Tenorite</th>
<th>Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>0.96583</td>
<td>0.32590</td>
<td>0.12914</td>
<td>0.51585</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.00506</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.16295</td>
<td>0.16295</td>
<td></td>
<td>0.0071</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.42833</td>
<td>0.16295</td>
<td>0.25828</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.12914</td>
<td></td>
<td>0.12914</td>
<td></td>
</tr>
</tbody>
</table>

Koenig's Analysis

<table>
<thead>
<tr>
<th>Molecular ratios</th>
<th>Malachite</th>
<th>Chrysocolla</th>
<th>Tenorite</th>
<th>Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>1.1177</td>
<td>0.0714</td>
<td>0.9669</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.0014</td>
<td>0.0714</td>
<td></td>
<td>0.9669</td>
</tr>
<tr>
<td>CO</td>
<td>0.0404</td>
<td>0.1428</td>
<td>0.0656</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.2488</td>
<td>1.767</td>
<td>5.983</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.0714</td>
<td>0.2856</td>
<td>0.9669, or</td>
<td>1.000</td>
</tr>
</tbody>
</table>

These results show that it is chemically possible for "copper pitch" to be a mixture and that the proportion of each mineral in the sample analysed by Koenig was 30.8% tenorite, 30.8% chrysocolla and 38.4% malachite, while the one analysed by Hunt contained 68.6% tenorite, 20% chrysocolla, and 11.4% malachite.

**METHOD OF STUDY**

A hand specimen of the material from Kalispell shows quartz, chalcopyrite, and limonite, with veins of
copper pitch in the chalcopyrite. From the appearance, it was thought that samples of pure "copper pitch" could be obtained by digging out these veins from a polished surface with a sharp needle. However, examination under high magnification showed that the "copper pitch" contained minute particles of chalcopyrite and limonite. With chalcopyrite and limonite both present, it would be impossible to calculate the mineralogical composition from a chemical analysis, because it would be necessary to know the percentage of iron present in each of these minerals.

Since, after removing these minerals it would be possible to calculate the sulfur to chalcocite and the remainder of the material would be "copper pitch", an attempt was made to separate some of the finely ground rejected material by flotation. This method of separation, however, was not sufficiently selective for, though a "copper pitch" concentrate was made, it still contained considerable amounts of chalcopyrite and limonite. To ascertain this fact, face briquets of bakelite were made of all flotation products.

Not being able to secure a pure sample for analysis, it was thought advisable to study the material thoroughly under a reflecting microscope and compare it with some material from Bisbee. Twenty polished sections of the material from Kalispell were made and one polished section
was made of material from near Bisbee. The latter specimen was purchased from Ward's Museum of Natural Science.

PREPARATION OF SPECIMENS AND PROCEDURE

In making the polished sections each specimen was first ground to a flat surface on a revolving glass plate using emery dust as an abrasive. The specimen was then ground further on two muslin-covered high speed wheels, the first using 600, the second 400 grain Alundum. A wheel of the same type but covered with felt was used with Livigated Alundum to give the final polish.

All etch tests were carried out according to the methods outlined by M. N. Short in "Microscopic Determination of the Ore Minerals", U. S. G. S. Bulletin 825. The basis of determination of the malachite and chrysocolla was the fact that when the light was shut off in the opaque illumination and the material lighted by an inclined light, they both showed up bright green due to reflected light. A drop of HCl quickly told if the material was chrysocolla or malachite.

RESULTS

Description of Material from Kalispell

A specimen of the material from Kalispell shows copper-stained quartz with irregular masses of chalcopyrite and "copper pitch" in it. On closer examination, masses of chrysocolla and limonite are seen. The chal-
copyrite is veined with "copper pitch" which causes it to be somewhat crumbly.

After polishing a specimen shows under low magnification areas of chalcopyrite in different stages of replacement by "copper pitch". Island and sea textures are common with the chalcopyrite forming the islands, as well as areas of apparently pure "copper pitch".

The chalcopyrite is easily distinguishable by its color and appearance and readily identified by the etch reactions. The "copper pitch", however, is not easily distinguished showing different shading. Under higher magnification this shading was found to be due to the presence of chalcocite as inclusions in the "copper pitch" (Figure 2, Plate 1) and as narrow borders around the chalcopyrite (Figure 1, Plate 1). It was very difficult to test either the "copper pitch" or the chalcocite but the following properties of the "copper pitch" were identified. It is a darker grey than the chalcocite without the bluish tinge and with a much duller luster. The etch reactions are: HNO₃ slowly stains the surface brown on most specimens, on others there is no reaction, HCl stains brown with the acid drop turning green, KCl, FeCl₃, KOH and HgCl₂ have no effect.

The etch reactions on the light bluish grey mineral identified as chalcocite might have been in error due to electrolytic effects set up when the acids cover more than
one mineral. If an electrolytic effect were set up, however, the change in reaction of the chalcocite should have been compensated for by a change in reaction in the other mineral. The other mineral was "copper pitch", and since no change in the etch reactions of the "Copper pitch" could be noticed, it was assumed that no electrolytic couples were set up.

Description of Material from Bisbee

A hand specimen of this material shows a kernel of cuprite with a shell of "copper pitch" and an outer shell of malachite which shows banding.

A polished section shows the same general relationship. In detail, however, masses of chrysocolla can be seen extending into the "copper pitch" from the cuprite contact. (See Figure 3, Plate 1). Under the microscope the banding was found to extend into the "copper pitch". To the naked eye, the boundary between the malachite and "copper pitch" appeared well marked, but under the microscope it moved toward the "copper pitch". Since banding represents a difference in composition which causes a change in color, it is possible that the malachite and "copper pitch" are in alternating bands which grow thinner towards the center of the kernel. This would explain the apparent shifting of the contact in as the magnification was increased, because the inclined light might
be at the right angle to cause more of it to be reflected by the malachite than would be reflected in ordinary light. Under a high magnification the "copper pitch" shows numerous inclusions (Figure 4, Plate 1). Some of the larger of these were identified and chrysocolla, malachite, and cuprite found to be the minerals making them up. Inclusions of chrysocolla were most numerous with malachite next and only a very few of the inclusions were composed of cuprite.

PARAGENESIS

The origin of the material from Kalispell is evidently the chalcopyrite. The chalcopyrite is altered to chalcocite and limonite or ferric sulfate which is carried away. The next step is the oxidation of the chalcocite to "copper pitch". The proof of this lies in the mineral relationships noticeable in Figure 1, Plate 1. The veins contain "copper pitch" in the center with bands of chalcocite on either side and a matrix of chalcopyrite. In other portions, the alteration has gone further and no chalcopyrite remains, the chalcocite inclusions show where chalcopyrite particles have been (Figure 2, Plate 1).

The banding of the material from Bisbee permits two possible explanations. The "copper pitch" could have been precipitated on the surface of the cuprite and then malachite later deposited or else the cuprite was oxidized to "copper pitch" and the banding was due to colloidal
precipitation. A study of the origin of this material would be very interesting and probably very useful.

CONCLUSIONS

Hunt and Kraus showed that from the view point of a chemical analysis "copper pitch" was probably a mixture of tenorite, chrysocolla and malachite. The present investigation has shown that this conclusion was the correct one and thrown some light on the character of the mixture.

Under the reflecting microscope, it is possible to see that "copper pitch" is made up of different minerals. Material from Kalispell shows minerals identified as chalcocite and tenorite, while that from Bisbee shows minerals identified as tenorite, chrysocolla and malachite. The occurrence of the impurities in the material from Bisbee is such that by picking a sample even under a binocular microscope, the amount of chrysocolla and malachite would be measured in percentage as great as those given by Hunt and Kraus.

From the above facts, the conclusion was reached that "copper pitch" is impure tenorite. The more common impurities being chrysocolla, malachite, chalcocite and possibly manganese oxide or silica. It was further evident that chrysocolla and malachite found by Hunt and Kraus as impurities in tenorite, or perhaps we should say mixed with tenorite to form "copper pitch", occurred
in the following manner: the chrysocolla as inclusions and irregular masses on the boundary between the "copper pitch" and cuprite; the malachite as inclusions and thin bands, so thin that the "copper pitch" appeared homogeneous under the naked eye, or even a bimocular microscope.
Figure 1

This is a photograph (X50) of specimen #2 from Kalispell. It shows chalcopyrite (Cp) veined by "copper pitch" (Cpi) with chalcocite (cc) forming bands between the chalcopyrite and "copper pitch". Near the center several residual masses of chalcocite can be seen.

Figure 2.

Figure 2 is a photograph (X200) of what was thought to be pure "copper pitch". It shows, however, small masses of chalcocite (cc) in the "copper pitch". The dark spots are probably pits. This was specimen #6 from Kalispell.

Figure 3.

This photograph (X20) of the specimen from Bisbee shows the cuprite (Cu), "copper pitch" (Cpi) and malachite (Mal). It also shows a mass of chrysocolla (cry) on the "copper pitch" cuprite boundary. The boundary of the "copper pitch" and malachite is shown by the pointer in the left hand corner.

Figure 4

Figure 4 is a photograph (X200) of the same specimen. The field is from the upper right of Figure 3 and shows an irregular mass of malachite in "Copper pitch".