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COPPER PITCH ORE.

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A jet black to brownish pitch-like material rich in copper is frequently encountered among the supergene minerals of copper deposits. It has a conchoidal fracture and when occurring in large enough pieces, closely resembles obsidian or even anthracite coal. It seems to vary in hardness from less than 3 to about 4 and is sometimes very brittle. It often grades into portions that are more or less sooty, thus increasing its resemblance to coal. It is frequently associated with copper oxide (cuprite) with comparatively small amounts or even no other copper minerals closely associated with it. (Analysis No. 1). Such specimens seem to possess the maximum hardness if we except those varieties which contain considerable chalcedony. In other cases, and more characteristically perhaps, it is associated with blue and greenish chrysocolla, malachite and limonitic material. Sometimes the mass appears rather streaked with the black, brown, blue and greenish material intermingled. Specimens of copper pitch are mostly opaque even in thin slivers though one sample from Katanga, Belgian Congo, while black in the hand specimen appeared quite transparent on the thin edges. This specimen seemed to grade into chrysocolla, perhaps with an excess of silica.

Not many analyses of this material have been published, its evident colloidal and impure nature serving to deter one in this endeavor. It is mentioned in most mineralogies sometimes being described under limonite and at others under chrysocolla. Thus in Naumann-Zirkil's *Elemente der Mineralogie* (1907, p. 505) it is stated that the mineral " . . . . scheint ein secundäres Gemenge von Eisenoxydhydrat mit dem Silicat Kupfergrün oder mit Kupferoxydul und Kieselsäure zu sein." Tschermak[1] also mentions it under limonite and describes it as an alteration product of copper ores and associated minerals, and states that it contains copper

[1] Tschermak, *Lehrbuch der Mineralogie*, **1905**, p. 466.

silicate. Niggli[2] also mentions it under limonite, and refers to the presence of P_2O_5 in some samples. Analyses in which phosphorus has been determined do not appear to be available, yet we believe it not to be an important constituent.

On the other hand, Des Cloizeaux[3] mentions it under chrysocolla and gives an analysis by Damour on material from Turjinsk in the Urals in which there is a high percentage of iron and silica. (Analysis No. 2). This probably was a mixture of chrysocolla and limonite. Both Hintze and Dana[4] describe it under chrysocolla but state that it is a mixture of copper silicate and limonite.

In the United States copper pitch is described, usually very briefly, as occurring in tne most important copper districts. Thus Weed[5] mentions it from the Butte District, Montana, but no analyses were made and the author was uncertain whether it corresponded to the Arizona material. He described it as a "lustrous coal-black or dark-brown crust associated with other copper ores." B. S. Butler[6] also mentions it from the San Francisco Region, Utah. He states: "It is probably variable in composition, but contains considerable amounts of copper, iron, manganese and water." Ransome[7] recognized manganese as an important constituent in the material from Globe, Arizona, as he reports under the heading "chrysocolla." He writes: "It varies widely in color from delicate apple green to turquoise-blue, to dark green, brown or black, the darker shades being apparently due in most cases to the presence of the oxide of manganese."

A more detailed investigation of some of the best American material, *i.e.*, the blackest and most coal-like, seems to show that at times iron is not an important constituent, and that even silica may be present in rather inconspicuous amounts. Thus Koenig[8]

[2] Niggli, *Lehrbuch der Mineralogie*, **1926,** p. 681.

[3] Des Cloizeaux, *Manuel de Mineralogie*, **1862,** V, I, p. 125.

[4] Hintze, *Handbuch der Mineralogie*, Bd. II, **1897,** p. 462. Dana, *System of Mineralogy*, **1892,** p. 699.

[5] Weed, Geology and Ore Deposits of the Butte District, Mont., *U. S. Geol. Sur., Prof. Paper. No.* **74,** p. 81.

[6] Butler, Geology and Ore Deposits of the San Francisco and Adjacent Districts, Utah. *U. S. Geol. Sur., Prof. Paper, No.* **80,** p. 98.

[7] Ransome, Geology of the Globe Copper District, Ariz., *U. S. Geol. Sur., Prof. Paper, No.* **12,** p. 123.

[8] Koenig, On the new Species Melanochalcite and Keweenawite, *Am. J. Sc.*, (4), **14,** 1902, p. 404.

analyzed material from Bisbee, Ariz., to which he gave the name of Melanochalcite, that contained only 0.07% iron oxide and 7.80% of silica. (Anal. No. 3). This type of copper pitch ore was further investigated by Hunt and Kraus.[9] These authors are not in favor of the carbono-silicate idea as there appears to be too small a percentage of silica. Recasting their own analysis as well as that of Koenig they find the Bisbee material corresponding to 30.8%

TABLE OF ANALYSES OF COPPER PITCH ORE

	No. 1. Guild. Bisbee.	No. 2. Damour. Urals.	No. 3. Koenig. Bisbee.	No. 4. Hunt. Bisbee.	No. 5. Lindgren-Hillebrand. Clifton-Morenci.	No. 6. Guild. Globe.	No. 7. Buehrer. Huerta Arriba.
SiO_2	2.95	17.95	7.80	4.31		24.64	5.75
Al_2O_3	0.00					3.10	
Fe_2O_3	0.64	50.85	0.07	0.22	4.00 (+Al & P.)	1.73	4.40
CuO	84.22	12.12	76.88	88.94	28.6	33.68	62.3
CaO	0.36					0.84	
ZnO	0.25		0.41	0.12	8.4	tr.	
MnO	0.28				21.20 (as MnO_2)	19.19	0.00
H_2O	6.91	20.55	7.71	4.48			
CO_2	5.17		7.17	1.78			
Insol.					22.8		
Ignition					13.7	17.76	
Total	100.78	101.47	100.04	99.85		100.94	

tenorite, 30.8% chrysocolla and 38.4% malachite according to Koenig's analysis, and 68% tenorite, 20% chrysocolla and 11.4% malachite, according to their analysis. (Anal. No. 4). The writer's analysis shows still less silica corresponding to a still less admixture of chrysocolla (Anal. No. 1). Furthermore Hunt and Kraus, in examining their material in a very fine powder form, found evidence of a mixture such as suggested by their recast analyses. They also show that Koenig's material was probably non-homogeneous though thought to be pure by him. The writer's material from Bisbee corresponds in appearance to that described by Koe-

[9] Hunt and Kraus, Composition of Melanochalcite, *Am. J. Sc.*, (4), 41, p. 211, 1916.

nig, Hunt and Kraus, and others except that the nodular masses are embedded in nearly white, hard kaolinized matter, practically free from greenish or bluish oxidation products. It surrounds centres of crystalline cuprite and certainly appears to be an alteration (hydration) product of it.

Lindgren has investigated copper pitch ore from the Clifton-Morenci District, Arizona.[10] Most of this material had been considered an impure chrysocolla, but Lindgren proved it to be entirely distinct from that mineral. (Anal. No. 5). He states: "As shown by the optical characteristics, however, they are not a mixture, and they certainly do not contain any chrysocolla. . . ." The amount of insoluble residue in the analysis of Lindgren and Hillebrand might indicate its presence, perhaps in solid solution. Limonite, however, cannot be considered as an important constituent in the Clifton-Morenci material as only 4% Fe_2O_3 ($+Al_2O_3$ and P_2O_5) is reported. This is also true of the two samples analyzed by the writer (Anal. Nos. 1 and 6). Here only 0.64% and 1.73% are found. In this respect, prehaps, the specimens differ somewhat from what had been described as copper pitch ore in many of the German texts.

Silica also would appear to be an unimportant constituent in certain types of this material as shown by one of the analyses of the writer. (No. 1). Only 2.95% SiO_2 was found. Therefore, in this case at least, it cannot contain any considerable quantity of chrysocolla.

Likewise in other important respects copper pitch minerals differ widely in composition, that from Bisbee containing practically no manganese, while the Globe and Morenci specimens show 19.19% (reported as MnO) and 21.2%, respectively, (reported as MnO_2). (Anal. Nos. 6 and 5.) Carbon dioxide also occurs in some types in quantities that cannot be neglected, although Hunt and Kraus refer this to malachite and have been able to detect this impurity in the fine powder. There seemed to be no particular evidence that it is present as a carbono-silicate as suggested by Koenig in 1902. The material from Bisbee analyzed by the writer contained 5.17% CO_2 by direct determination. The material was very homogeneous and associated only with cuprite which occurred in the centre of nodules of copper pitch, the whole being embedded in hard nearly

[10] Lindgren, Copper Deposits of the Clifton-Morenci District, Arizona, *U. S. Geol. Sur., Prof. Paper, No.* 43, 1905, p. 115.

white kaolinized rock. There was no evidence of copper carbonate which might have made its appearance as green or blue stains in the immediate vicinity. Yet the specimen effervesced lively when treated with hot hydrochloric acid. This percentage of CO_2 should, when recast to malachite, show a sufficient amount of the carbonate to be easily seen by the lens, unless, of course, it be in the form of a solid solution or colloidal mixture, an explanation which seems to be the most probable.

The other sample analyzed by the writer (No. 6) is quite different in mode of occurrence as well as in composition. It appears in large masses sometimes the size of a fist, yet consisting of uniform, pure black pitchy-like material with conchoidal fracture. This may grade into streaks of brown still possessing the pitchy appearance and conchoidal fracture, or it may pass into dark greenish or bluish streaks of irregular outlines. It is further found mingled with more or less ocherous limonitic material or closely associated with crystalline azurite and malachite. Even clean light blue patches of chrysocolla may appear and grade off into the black or brownish pitchy types. Black sooty areas are also to be found which soil the fingers and react strongly for manganese.

The specimen from Globe, Arizona, analyzed by the writer (No. 6) was taken from material such as is described above, the blackest portions possessing the best conchoidal fracture being chosen. The material selected did not soil the fingers appreciably and does not effervesce with HCl. It would seem from the analysis to be a mixture (probably) of hydrous oxides of manganese and copper with, perhaps, some chrysocolla. This material corresponds to the type partially analyzed by Lindgren and Hillebrand (No. 5) from the Clifton-Morenci District.

Specimens received from Huerta Arriba, Province of Borgos, Spain, are of particular interest because of the large quantity of the material represented. Usually copper pitch ore, although occurring in most copper deposits that have been subjected to considerable oxidation, is found only in small patches. That described from Globe, Arizona, as occurring in sizes up to three or four inches without variation from the pure black pitchy material, seems to be about the limit so far as individual pieces are concerned. At Huerta Arriba, however, the material was said to be obtained for a time in car-load lots. This was at first thought by the observer[11]

[11] Courtenay DeKalb, personal communication.

to be some type of coal and a test was even made in a convenient forge. A partial analysis made by Dr. T. F. Buehrer is given in table No. 7. On close inspection this material shows numerous but very inconspicuous spots of some greenish copper mineral probably malachite. The large masses, however, much resemble coal though more friable than many of the other samples examined. This type of copper pitch seems to correspond very closely to the Bisbee variety. Carbon dioxide though not determined seemed to be present in considerable quantities.

RÉSUMÉ

Copper pitch ore, as described by various writers, seems to be a mixture of several hydrous oxides, often with silicates and carbonates, in a more or less colloidal state.

The foregoing investigation seems to emphasize the possibility of this substance containing rather insignificant quantities of both iron and silica. Therefore, the tendency to group this mineral with either limonite or chrysocolla should not be too greatly stressed.

It ordinarily occurs only in small quantities as incrustations and streaks in oxidized material, though in one case (Huerta Arriba, Spain) it was reported to be found for a time in car-load lots.

It may be classified into the following types according to the relative amounts of the oxides present:

(1) A more or less colloidal mixture of the hydrous oxides of copper and iron. This seems to apply more nearly to those types described in the German texts and frequently listed under limonite.

(2) A mixture of oxide of copper and chrysocolla. This applies especially to those specimens, containing considerable silica, and seem to grade into chrysocolla.

(3) A mixture of the oxides, more or less hydrated, of copper and manganese. Silica may also be present in considerable quantities.

(4) A hydrous oxide of copper. These varieties (melanochalcite) have considerable carbon dioxide which is difficult to account for. If present as copper carbonate it must be colloidally mixed.

(5) A fifth type might be mentioned to cover those types where the copper pitch and the admixed chrysocolla grade into chalcedonic varieties. These become so light in color and seem to grade off into chrysocolla in such a manner that they may well be considered as variations of that mineral.