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A SUMMARY OF IDEAS ON THE ORIGIN OF NATIVE COPPER DEPOSITS[1]

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CONTENTS

ABSTRACT

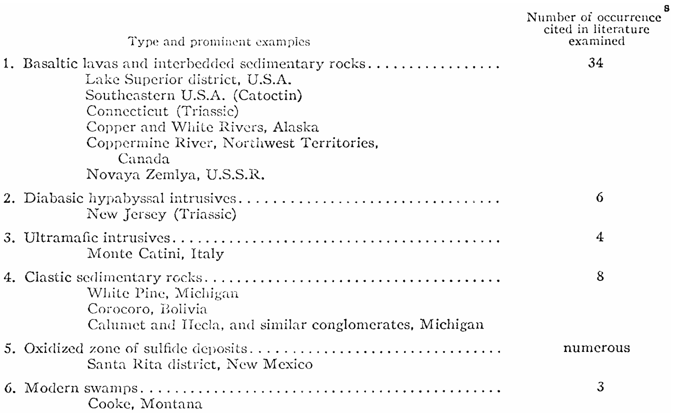
Native copper occurs in a wide variety of environments that includes mafic lavas, hypabyssal diabasic intrusives, ultramafic intrusives, clastic sedimentary rocks, and the oxidized zone of sulfide deposits. Native copper is the predominant copper mineral in mafic lava flows, best exemplified in the Lake Superior region, and in some sedimentary rocks, but it is typically subordinate to sulfide copper in other types of deposits.

Possible natural origins of native copper include: precipitation from sulfide-bearing hydrothermal solutions in rocks containing ferric oxide; deposition from sulfur-deficient magmatic or hydrothermal solutions; deposition from meteoric or hydrothermal chloride solutions in the presence of calcite, prehnite, or zeolites; precipitation from hydrothermal solutions by ferrous salts; organic precipitation from meteoric waters; reduction of copper sulfides by meteoric waters in the zone of oxidation; reduction of primary copper sulfides by later hydrothermal solutions.

INTRODUCTION

COPPER, silver, and gold are distinguished among metals in the earth's crust by their widespread occurrence and local abundance as the native metal. The commonness of native copper in Nature is rather surprising in view of the ease with which it combines with other elements, particularly sulfur, to form sulfides, carbonates, silicates, and other compounds. Also remarkable is the diversity of environments in which native copper occurs. The geologic associations of native copper, as shown in Table 1, range from mafic extrusives and intrusives to clastic sedimentary rocks, and to contemporary zones of weathering and meteoric waters.

TABLE 1
GEOLOGIC ASSOCIATIONS OF NATIVE COPPER



Type and prominent examples	Number of occurrences cited in literature examined
1. Basaltic lavas and interbedded sedimentary rocks	34
Lake Superior district, U.S.A.	
Southeastern U.S.A. (Catoctin)	
Connecticut (Triassic)	
Copper and White Rivers, Alaska	
Coppermine River, Northwest Territories, Canada	
Novaya Zemlya, U.S.S.R.	
2. Diabasic hypabyssal intrusives	6
New Jersey (Triassic)	
3. Ultramafic intrusives	4
Monte Catini, Italy	
4. Clastic sedimentary rocks	8
White Pine, Michigan	
Corocoro, Bolivia	
Calumet and Hecla, and similar conglomerates, Michigan	
5. Oxidized zone of sulfide deposits	numerous
Santa Rita district, New Mexico	
6. Modern swamps	3
Cooke, Montana	

The bibliography on native copper is extensive, but most of the authors limit their discussions to individual deposits. Lindgren (70; 71, p. 418-421, 514-523), however, gives careful consideration to the general relations and probable mode of origin of the most important types of native copper deposits. The present author has attempted In this paper to review briefly and evaluate, in the light of his experience, the various facts and theories that have been recorded concerning the occurrence and origins of this mineral. This is not a comprehensive review, but rather an appraisal of the information available as indicated by the included bibliography.

The association of native copper with basaltic lavas is common and widespread, as indicated in Table 1 by the number of occurrences cited in the literature examined (see Bibliography). In many lava sequences, native copper occurs as low-grade disseminations or small isolated masses. In several districts the deposits approach commercial size and grade, and on the Keweenaw Peninsula in the Lake Superior district six deposits in lavas have profitably yielded, together, over 5 billion pounds of copper in the past 100 years.

Native copper is a prominent constituent of deposits in clastic sedimentary rocks that are locally sufficiently rich and large to be important commercially, as for example in the White Pine deposit in the Nonesuch shale of Michigan, and at Corocoro, Bolivia. The Calumet and Hecla conglomerate, in the Lake Superior district, has yielded over 4 billion pounds of copper; this conglomerate lies between two lava flows and may have more in common with the deposits in lavas than with those in sediments. In the remaining types of

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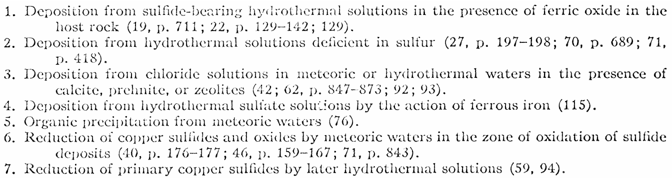
occurrence, native copper does not form large ore bodies.

The wide variety of conditions under which native copper may form indicates that it is stable within an appreciable range of physical and chemical environments, including: 1) those that accompany the cooling of a lava flow; 2) low to medium temperature hydrothermal environments; 3) ground water in the lower part of the zone of oxidation; 4) reducing waters in the bottoms of lakes, swamps, and shallow seas.

TABLE 2
POSSIBLE NATURAL ORIGINS OF NATIVE COPPER



1. Deposition from sulfide-bearing hydrothermal solutions in the presence of ferric oxide in the host rock (19, p. 711; 22, p. 129–142; 129).
2. Deposition from hydrothermal solutions deficient in sulfur (27, p. 197–198; 70, p. 689; 71, p. 418).
3. Deposition from chloride solutions in meteoric or hydrothermal waters in the presence of calcite, prehnite, or zeolites (42; 62, p. 847–873; 92; 93).
4. Deposition from hydrothermal sulfate solutions by the action of ferrous iron (115).
5. Organic precipitation from meteoric waters (76).
6. Reduction of copper sulfides and oxides by meteoric waters in the zone of oxidation of sulfide deposits (40, p. 176–177; 46, p. 159–167; 71, p. 843).
7. Reduction of primary copper sulfides by later hydrothermal solutions (59, 94).

A number of geologists have investigated or considered the mode of formation of native copper in these very diverse environments. The principal theories of origin that have been published are summarized in Table 2. All the postulated origins arc based upon the geologic characteristics of specific individual natural occurrences, and the chemical explanations for several have been substantiated experimentally. The widely varied origins are most clearly illustrated by small isolated occurrences of native copper. The largest deposits, namely those in the Lake Superior district of Michigan and those at Corocoro, Bolivia, are more complex, and the available geologic data are compatible with more than one theory of origin.

In the following paragraphs the different types of native copper occurrence under the headings listed in Table 1 will be discussed.

NATIVE COPPER IN BASALTIC LAVAS

Scattered throughout the world are more than 30 areas of basaltic lavas that contain native copper, some of which occurs in deposits of potential commercial importance. The individual occurrences are listed in Table 3. Certain characteristics common to most of the areas suggest a close genetic relationship between native copper and mafic lavas. In 15 of the areas listed in Table 3, for example, the authors report that certain flows contain moderate amounts of finely disseminated primary native copper, whereas the remaining flows contain little or no visible copper. This concentration of native copper in certain individual flows of a sequence serves to identify these flows in the same manner that other unique compositional or mineralogic features characterize other individual flows. Thus the copper content and mode of occurrence appear to depend on the source and petrologic history of the flow just as do other Inherent peculiarities of the rock. Another common characteristic is that copper, both as native copper and as copper sulfides, is most abundant in the pegmatitic and vesicular parts of the flows (17, p. 512, 517, 525; 22, p. 46; 27, p. 177, 183, 197). Also, the mineralogy of the copper occurrences Is similar everywhere. The secondary minerals associated with native copper are, in approximate order of decreasing abundance, calcite, quartz, epidote, chlorite, prehnite, chalcedony, zeolites, and datolite.

TABLE 3
NATIVE COPPER OCCURRENCES ASSOCIATED WITH BASALTIC LAVAS

Locality	Reference
Canadian Arctic	
Coppermine River	Douglas (35), O'Neill (91)
Bathhurst Inlet	Duncan (36), Norrie (89)
Labrador, Canada	
White River, Alaska	Knopf (58)
Copper River, Alaska	Schrader and Spencer (105), Moffitt (81, 82), Bateman and McLaughlin (7)
Cap d'Or, Nova Scotia	Dawson (33)
First Mountain, New Jersey	Lewis (66, 67), Weed (128)
Connecticut	Butler, and others (22)
Southeastern U.S.A. (Catoctin)	Watson (127), Stose (116), Weed (128)
Lake Superior district, Michigan	Lane (62), Butler, and others (22)
Northeastern Oregon	
Triassic lavas	Lindgren (68)
Miocene lavas	Waters, A. C. (personal communication)
Mt. Meadows, Lassen County, Calif.	Kinkel, A. R., Jr. (personal communication)
Northern California (metamorphosed basalts)	Turner (12)
Comobabi Mountains, Arizona	Butler, and others (22)
Baggs Creek, Montana	Billingsley and Grimes (14)
Saõ Paulo, Brazil	Hussak (56)
Parana, Brazil	Leonardos (65)
Tolima, Colombia	Reymond (99)
Faroe Islands	Cornu (26)
Dalane, Norway	Neumann (86)
Serbia, Yugoslavia	Lazarevic (64)
Oberstein, Germany	Hintze (53)
Wielki, Mydsk, Volhynia, Poland	Malkowski (77)
Glarus, Switzerland	Amstutz (4)
Stirling, Scotland	Hintze (53)
Novaya Zemlya, U.S.S.R.	Voit (125), Alferov (3)
Urals, U.S.S.R.	Zavaritsky (134)
Siberian lava platform, U.S.S.R.	Moor (83)
Dzhida, Trans-Baikal, U.S.S.R.	Beck (8, 9)
Komandorski Islands, U.S.S.R.	Morozewicz (85)
Szechuan and Yunnan, China	Chu (25)
Queensland, Australia	Beck (9)
New Guinea	Beck (8)

Where sulfides are present in basaltic lavas, chalcocite, the sulfur-poor sulfide, is much more common than chalcopyrite or bornite, which suggests a deficiency of sulfur in the lava environment. Sulfides are reported to be relatively abundant in 10 localities (northeastern Oregon; New Jersey; Connecticut; Virginia; White River, Alaska; Szechuan and Yunnan, China; Tolima, Colombia; Biloela, Queensland; Oberstein, Germany).

The copper in mafic lavas may be classified into two general categories: 1) primary disseminations of copper, mostly in the native state, that crystallized as the lava solidified; and 2) epigenetic concentrations of native copper that are in or adjacent to permeable zones in the lava sequence.

The two types of copper occurrence are well illustrated in the Lake Superior copper district, although it may not always be possible to determine in which category a particular grain of copper belongs. The massive rock in the interiors of the flows contains from 10 to over 400 ppm (parts, per million) of copper, dominantly as interstitial grains finely disseminated through the rocks (17, 18, 27, 28, 29). Certain flows are characteristically rich in disseminated copper and others are lean; moderate concentrations of copper are found in pegmatitic segregations that occur in some of the flows.

In the many polished sections examined microscopically, the visible copper mineral is most commonly the native metal (28, p. 57-58). Comparison of rock analyses with spectrographic analyses of trace elements in mineral separations of the lavas, however, indicates that a third or more of the primary copper is concentrated in individual minerals and may have entered the crystal lattice of certain silicates and oxides (30). This copper is abundant in certain minerals and scarce in others. In seven analyzed rock samples, ranging in composition from basalt to pegmatite and granophyre, copper is most abundant in magnetite, where it ranges from 200 to 880 ppm. The remaining minerals contain copper in the following amounts: ilmenite, 90 to 300 ppm; augite, 51 to 320 ppm; chlorite, 50 to 280 ppm; plagioclase, 20 to 73 ppm.

The distribution of the disseminated copper in the flows and its concentration with other chemically related elements (such as Fe, Ti, P, Mn, V) in the pegmatitic facies and in certain minerals, indicates that this trace copper crystallized directly from the basaltic magma or its residual solutions, and a logical explanation of its native state is that the depositing medium was deficient in sulfur. The writer (27, p. 197-198) has followed Lindgren (70, p. 689; 71, p. 418, 420-421) in suggesting that sulfur was lost to the lava as a gas during the extrusion and crystallization process. This explanation of the native state seems to have more universal application than the theory of reduction by ferric oxide in the host rock (see 1, Table 2), inasmuch as native copper occurs in many lavas that do not have red, oxidized flow tops or interiors. This sulfur deficiency in lavas is in contrast to the situation in mafic intrusive bodies where disseminated copper typically occurs as a sulfide, either chalcopyrite or bornite. Though many exceptions can be cited, native copper is characteristically associated with lavas, and copper sulfides with intrusive bodies; these associations are sufficiently universal to suggest strongly that where native copper is concentrated in or adjacent to lavas, the ultimate source of this copper may be the lava itself, rather than some remote intrusive rock.

Native copper also occurs as epigenetic concentrations in or adjacent to permeable zones in lava sequences such as those in the Lake Superior copper district. The commercial deposits of this district are found principally in (1) the fragmental layer, once rubbly, but now filled with secondary minerals, at the tops of certain lava flows; (2) conglomerates lying between some of the lava flows; and (3) veins (fissure deposits) that cut the sequence of lava flows almost at right angles to the layering. The deposits have been described In detail by a number of geologists (19, 22, 62, 96, 97) and need not be elaborated here. That the deposits are epigenetic and their location controlled very largely by permeability of the host rocks seems well demonstrated (19, 22). The ultimate source of the copper, however, is less clear. The principal theories and arguments that have been presented can only be touched on in this brief review of the types and outstanding characteristics of native copper deposits. The writer and his colleagues are preparing a more complete discussion for their report on the Michigan copper district.

Pumpelly (96, 97), Wadsworth (126), and Lane (62, p. 847-873) have suggested that copper present in minute amounts as a primary constituent in lavas or associated clastic sedimentary rocks of the Lake Superior district was leached from these rocks by surface waters and precipitated in permeable zones (fissures, vesicular and brecciated flows tops, interbedded conglomerates and sandstones) during downward circulation of the waters. Lane (62) assumed that the water was primarily sea water, imbibed into the cooling lava pile.

Smyth (111), Butler and others (22, p. 118-145), and Broderick and others (19) have, on the other hand, postulated a hidden body of magma at depth as the source of copper-bearing emanations, which ascended along permeable zones in the tilted lava sequence and deposited copper where conditions were favorable. Butler and others (22, p. 118-145), and Broderick and others (19) postulate that the sulfide-bearing solutions reacted with wall rocks (flow tops and interbedded sedimentary rocks) rich in ferric iron with the result that the iron was reduced, the sulfur oxidized, and native copper precipitated. Wells (129, p. 40-41) tried unsuccessfully to reproduce this reaction experimentally. Native copper has been precipitated experimentally, however, by the reducing action of ferrous sulfate on a solution of copper sulfate at 200° C (115, p. 647) and also by cooling cuprous sulfate solutions (129, p. 39).

Lindgren (71, p. 525) pointed out the following difficulties presented by the theory of magmatic origin: (1) the enormous amount of magmatic water required; (2) the unsatisfactory explanation of the chemistry of the proposed process of copper deposition—copper could be formed experimentally only in the presence of solutions of improbable acidity; and (3) no fissure veins with similar mineralization and oxidation of sulfur are known from other parts of the world. He cites the probability that strongly active hot waters ascending through thousands of feet of basaltic rock will dissolve appreciable quantities of trace copper, and elsewhere (71, p. 517) says that "the suggestion that the whole or a part of the copper in the deposits was extracted by waters from the rock itself almost forces itself upon the observer."

As suggested above, the typical native state of copper in lavas in general points strongly to the lavas themselves as the source for the native copper that was later concentrated in the copper deposits in the Lake Superior district. The geometry of several deposits in the Lake Superior district strongly supports the view that the copper-bearing solutions ascended to the point of deposition (19, p. 696-697; 22, p. 115-116). Presumably, such ascending waters would be heated, with or without the assistance of magmatic heat. If the interstices of the porous flows tops and the interbedded sediments were filled with ground water as the lava series accumulated, many cubic miles of water were carried to depths from which they could later be driven out by heating and compaction. (W. S. White, personal communication.) Connate water of this origin seems a reasonable alternative to magmatic water, and, unlike magmatic water, need not contain any significant amount of sulfur to be explained away. The high chloride content of the present mine waters in the Michigan district suggests the possibility that the ore-bearing solutions may have been chloride rather than sulfide waters (62, p. 774—846). Copper would be considerably more soluble in chloride solution than in sulfide; native copper has been precipitated from copper chloride solutions at 200-250° C in the presence of prehnite, calcite, or zeolites (42, 92, 93).

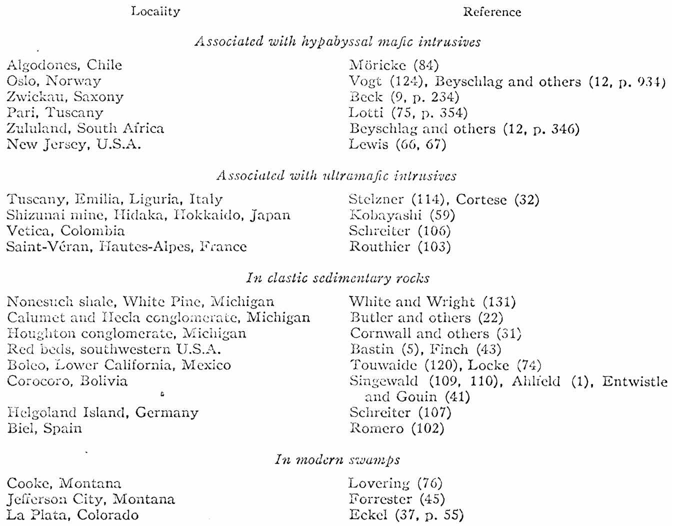
To sum up, the native copper deposits of the Keweenaw Peninsula, Michigan, were almost certainly formed in permeable channelways by hot ascending solutions, whose composition has not yet been demonstrated. The native state of copper strongly suggests its derivation from the lavas themselves; lavas all over the world are characterized by the native state of the traces of copper that they contain, a state that is presumably due to loss of sulfur during extrusion. It does not seem necessary to postulate a magmatic source for much or all of the solutions that deposited the copper; connate waters, driven upward by heating and crushing in the more deeply buried parts of the lava series, provide a more reasonable alternative. It would appear, in fact, unlikely that the permeable lava sequence with interbedded water-deposited sediments was downfolded and buried without the entrapment of considerable amounts of connate water. Other native copper concentrations that may well represent a similar reworking during slight to moderate metamorphism are well illustrated in the Nicolai greenstone of the Copper River district of Alaska (7, 79, 81, 82, 105) and in the lavas of the Catoctin of eastern United States (116, 127, 128).

NATIVE COPPER IN HYPABYSSAL MAFIC INTRUSIVES

Hypabyssal intrusions of diabase, gabbro, and related rocks locally contain small amounts of native copper generally associated with copper sulfides. Several occurrences are listed in Table 4. The native copper occurs as disseminated grains and as fillings of seams and vesicles with calcite and prehnite. At Zwickau, Saxony, and in New Jersey at Arlington and New Brunswick the copper occurs in disseminations and veins in tuffs, sandstones, and shales near intrusions of diabase or basalt. The host rocks in these occurrences are commonly bleached around the copper.

Sulfides predominate in these intrusions, but the local occurrence of disseminated native copper indicates a slight deficiency of sulfur when the copper crystallized (probably during the deuteric stage). A shallow depth of Intrusion probably permitted the volatile constituents, including sulfur, to escape rather freely. In the New Jersey deposits, Lewis (66, 67) considered that magmatic solutions containing cuprous sulfate and ferrous sulfate deposited native copper on cooling.

TABLE 4
NATIVE COPPER OCCURRENCES



Locality	Reference
Associated with hypabyssal mafic intrusives	
Algodones, Chile	Möricke (84)
Oslo, Norway	Vogt (124), Beyschlag and others (12, p. 934)
Zwickau, Saxony	Beck (9, p. 234)
Pari, Tuscany	Lotti (75, p. 354)
Zululand, South Africa	Beyschlag and others (12, p. 346)
New Jersey, U.S.A.	Lewis (66, 67)
Associated with ultramafic intrusives	
Tuscany, Emilia, Liguria, Italy	Stelzner (114), Cortese (32)
Shizunai mine, Hidaka, Hokkaido, Japan	Kobayashi (59)
Vetica, Colombia	Schreiter (106)
Saint-Véran, Hautes-Alpes, France	Routhier (103)
In clastic sedimentary rocks	
Nonesuch shale, White Pine, Michigan	White and Wright (131)
Calumet and Hecla conglomerate, Michigan	Butler and others (22)
Houghton conglomerate, Michigan	Cornwall and others (31)
Red beds, southwestern U.S.A.	Bastin (5), Finch (43)
Boleo, Lower California, Mexico	Touwaide (120), Locke (74)
Corocoro, Bolivia	Singewald (109, 110), Ahlfeld (1), Entwistle and Gouin (41)
Helgoland Island, Germany	Schreiter (107)
Biel, Spain	Romero (102)
In modern swamps	
Cooke, Montana	Lovering (76)
Jefferson City, Montana	Forrester (45)
La Plata, Colorado	Eckel (37, p. 55)

NATIVE COPPER IN ULTRAMAFIC INTRUSIVES

The ultramafic intrusives at the locations listed in Table 4 contain small amounts of native copper. The most common occurrences are in Tuscany, Emilia, and Liguria, Italy, where a number of serpentinite intrusives with associated diabase and gabbro are found (32). There the largest copper deposits, of which Monte Catini is the best known, occur in the larger intrusions and consist predominantly of slickensided bodies of massive chalcopyrite and bornite sheathed in crusts of chalcocite and native copper. Native copper also is disseminated and in small masses near the sulfide bodies. The serpentinite has been locally reddened near the native copper (114). Primary chalcopyrite and bornite segregations probably were altered to chalcocite and native copper by hydrothermal solutions that also oxidized the serpentine. Picruccini (94) believes that the formation of native copper was related to the oxidation of ferrous iron in a sulfate solution.

At the Shizunai mine, Japan, balls of native copper weighing as much as 200 kilograms (440 pounds) occur at the margin of a serpentinite body in the wall rock and in clays derived from weathering. Kobayashi (59) believes that the native copper was formed by secondary enrichment by ascending hydrothermal solutions. At Vetica, Colombia, veinlets of native copper with quartz and epidote occur in serpentinized pyroxenite. Schreiter (106) considers that the copper mineralization was related to serpentinization, and that the reduction of copper was effected by ferrous salts in hydrothermal solutions.

The similar characteristics of all the native copper occurrences in ultra-mafic intrusives indicate a common process of formation, namely, the reduction of older, possibly magmatic copper sulfides by hydrothermal solutions. The hydrothermal solutions probably acquired ferrous iron as they traversed and serpentinized the peridotite. The locally reddened rock around the copper masses at Monte Catini indicates a reaction between copper sulfide segregations and hydrothermal solutions containing ferrous iron that produced ferric oxide and native copper (94).

NATIVE COPPER IN CLASTIC SEDIMENTARY ROCKS

Copper deposits in sandstones and shales, commonly far removed from igneous rocks, are important in widely scattered parts of the world. The literature on these deposits is voluminous and has been summarized by Lindgren (71, p. 403-417), Bastin (5, p. 411-429), Yagovkin (132), and others. For the most part these deposits consist predominantly of copper sulfides. In some deposits native copper is a minor constituent, and in a few it is important. Only the deposits containing native copper are listed in Table 4 and will be discussed here.

One of the largest and commercially most important sedimentary copper deposits with native copper is the White Pine deposit, which lies west of the main Lake Superior native copper district, near Ontonogan, Michigan. Two to five thinly laminated to massive black shale beds, each ranging from 2 inches to 4 feet in thickness, in the lowermost 25 feet of the gently dipping Nonesuch shale, contain disseminations of chalcocite with minor amounts of native copper. As individual beds are followed toward the margins of the ore deposit, they first lose their native copper, then their chalcocite, and finally they become sparsely pyritic. The ore averages slightly over 1 percent copper. The abundance of copper and the ratio of native copper to chalcocite shows no apparent relationship to structure or permeability. White and Wright (131) believe that this deposit is essentially syngenetic and that the copper was de-posited at or soon after the time of deposition of the shale in which it occurs. Native copper in the chalcocite ore indicates either reducing conditions at the time of deposition, a deficiency of sulfur in the depositing waters, or later reduction by organic processes.

Sandstone beds below and within the shale sequence of White Pine contain copper, mostly as the native metal, whose distribution is very clearly related to structure. This copper is almost completely restricted to the southwest part of an anticline, just northeast of a major fault—the White Pine fault. It probably represents copper leached from shale on the downthrown side of the fault and deposited in permeable sandstone beds on the upthrown side, after hydrothermal transport up the fault zone, but a more deep-seated source for this copper is not ruled out (131, p. 706-708).

Other sedimentary copper deposits that contain native copper, among other copper minerals, are found at Biel, Spain (102), Helgoland, Germany (107), the Red Beds of southwestern United States (5, 43), Corocoro, Bolivia (1, 41, 109, 110), and Boleo, Lower California (74, 120). Native copper is only a minor mineral in the Red Beds and may be due to oxidation of original sufides (see: Native copper in oxidized ores). Native copper occurs only below the ground-water table at Boleo. The Biel and Helgoland deposits were probably deposited from circulating meteoric waters. Touwaide (120) believes that the clay beds at Boleo were mineralized by circulating connate waters that picked up copper from the interbedded tuffs.

The deposits of Corocoro, Bolivia, are of interest as the principal locality, outside of the Michigan district, where the native metal is a major ore mineral, though chalcocite has been the principal ore mineral for the last 35 years. The genesis of these deposits has been discussed at length by Singewald and Berry (110) and, more recently, by Entwistle and Gouin (41). The host rocks of the deposits are reddish to yellow or white terrestrial shales and sandstones that belong to two late Tertiary series, the so-called Ramos and Vetas. Entwistle and Gouin (41) describe an unconformity that establishes the Ramos as the older. Native copper is the principal ore mineral in the Ramos, and it was abundant in the oxidized zone, at least, of the Vetas. All the mine workings in the Ramos are probably within 200 meters of the pre-Vetas erosion surface, and Entwistle and Gouin suggest that the native copper in the Ramos may occur in a fossil zone of oxidation. Despite the fact that the only igneous intrusives in the area probably are older than the sediments, Singewald and Berry (110, p. 80) consider that the source of the mineralizing solutions is an underlying dioritic magma. Entwistle and Gouin (41) note the absence of alteration related to concentrations of chalcocite in reddish beds of the Vetas, the lack of relationship to faults or fractures, and the coincidence of ore shoots with channels in the sandstone beds. They suggest that the sulfide copper in the Vetas may be largely syngenetic, derived from erosion of older deposits in the subjacent Ramos.

The case for a syngenetic origin of even the deposits in the Vetas is far from conclusive. On the other hand, though the deposits may well be epigenetic, there is nothing positive in favor of a magmatic origin. It should be noted that the chief gangue minerals of the deposit, other than the rock minerals are gypsum, barite, and celestite, all typical constituents of gypsiferous beds such as might be expected in a red-bed sequence. The case for a magmatic source of the mineralizing solutions rests heavily on the extent of one's conviction that metals in such solutions are prima facie evidence of magmatic ancestry (110, p. 80).

The theory that magmatic sulfide solutions have been oxidized in hematitic host rocks to precipitate native copper has been advocated for both the Michigan copper deposits and for those at Corocoro, and the association of red host rocks and native copper at each place has been made an important element in arguments for this process at the other place (19, p. 711-712, 716-717; 22, p. 124, 130, 137, 142; 109). If, as Entwistle and Gouin (41) suggest, the native copper at Corocoro actually represents a mineral of modern and fossil surface oxidation zones, the mutual support of all arguments based on comparison of deposits in the two places may be invalid.

NATIVE COPPER IN OXIDIZED ORES

Native copper quite commonly occurs in small amounts in the weathering zone of sulfide deposits. In the sulfide ores of western North America, native copper is a common minor constituent of the oxidized zone, and it occurs directly above the zone of secondary chalcocite enrichment. Emmons (40, p. 176-178) and Lindgren (71, p. 842-844) discuss in general terms the occurrence of metallic copper in weathering zones, and Emmons (40, p. 199-251) describes the weathering effects in many hypogene deposits. One of the largest native copper deposits of this type was found in the Santa Rita district, New Mexico (72, p. 61-62, 306, 315-317), where native copper production in early days of the district amounted to millions of pounds.

Oxidation effects arc most pronounced in the weathering zone of hypogene sulfide deposits because of the normal abundance of pyrite that dissolves in ground water to form the powerful reagents, sulfuric acid and iron sulfate. Native copper and its oxides and carbonates are also found in oxidized sedimentary copper ores, as, for example, at Naukat (2, p. 467-485; 60) and Dzezkazgan (133) in central Asia. Under appropriate conditions, any copper-iron sulfide deposit may develop native copper in its oxidation zone.

In regard to the manner in which native copper is formed in weathering zones, Lindgren (71, p. 843) and Emmons (40, p. 176) state that in the oxidation of chalcocite deposits, native copper is developed from cuprite by the action of ferrous sulfate as follows:

$$Cu_2O + 2FeSO_4 + H_2SO_4 = 2\ Cu + Fe_2SO_4)_3 + H_2O$$

Also, native copper may be formed directly from chalcocite by the action of ferric sulfate:

$$Cu_2S + 3Fe_2\ (SO_4)_3 + 4H_2O = 2\ Cu + 6FeSO_4 + 4H_2SO_4.$$

Garrels (46) has recently discussed, in more or less quantitative terms, the chemical environment in the zone of oxidation and secondary enrichment of sulfide deposits. He considers the reactions in the weathering zone to be dependent almost entirely on the *p*H and the oxidation-reduction potential of the environment. Copper, he believes, dissolves near the surface by oxidation of the sulfide to sulfate. Thence it migrates downward, precipitating en route in a variety of minerals, including native copper, as the environment changes from oxidizing at the surface to reducing at depth. The native copper stability field, dependent primarily on the oxidation-reduction potential, lies between the field of cuprite (Cu_2O) and that of chalcocite (Cu_2S). Accordingly, native copper should and, in fact, commonly does occur most abundantly near the base of the zone of oxidation and just above the zone of secondary chalcocite enrichment.

NATIVE COPPER IN MODERN SWAMPS

Three descriptions of modern deposition of native copper in sedimentary environments have been published. Forrester (45) describes a native copper deposit in a swamp near Jefferson City, Montana. The copper occurs in peat muck, bog iron, and associated alluvial gravels. The reducing environment of the peat and bog-iron swamp has precipitated native copper from percolating ground water. Copper is leached from oxidized outcrops of epigenetic veins upstream in rocks of the Boulder batholith. It is carried downstream as copper sulfate until it reaches the reducing environment of the swamp.

Galbraith (in Eckel and others, 37, p. 55) describes a similar deposit of native copper in a swamp near La Plata, Colo. Ground water that has percolated through rocks containing disseminated pyrite and chalcopyrite drains into the swamp, which is about half an acre in extent. Black muck in the swamp, as much as 5 feet thick, contains numerous irregular nodules and grains of native copper. The muck also contains nodules of ferrous sulfide (troilite ?). Galbraith believes that these minerals are precipitated by reactions between organic matter and copper and iron sulfates in the swamp waters.

A third modern deposit of native copper occurs near Cooke, Mont., and is described by Lovering (76). This deposit is in a bog near the headwaters of Clarks Fork in a glacial valley. The bog contains thin beds of black muck, full of organic remains, interlayered with sand and gravel. Native copper occurs only in the muck, where it ranges In size from minute specks to lumps more than an inch in diameter. The surrounding upland is well mineralized, and several bodies of pyritic copper ore crop out half a mile above the bog. Lovering believes that copper, derived from the oxidation of these outcrops, is carried downward as cupric sulfate by ground water until it reaches the bog where the copper is precipitated by organic material. He produced metallic copper experimentally from copper sulfate solutions by the action of bacteria from the bog. His experiments indicated that the native copper formed by the reaction of the waste products of bacterial metabolism with the solution.

CONCLUSIONS

This review of the literature on native copper deposits reveals not only that native copper occurs in a wide variety of environments, but also that the processes of formation of the mineral must likewise be notably varied. The precipitation of native copper by the reaction of reducing materials in swamps with copper-bearing circulating surficial waters is demonstrated by present day observable processes. Not actually observable, but nevertheless quite certain, is the process of native copper formation in the oxidation zones of sulfide deposits by reactions taking place in circulating ground waters.

The origin of native copper in clastic sedimentary rocks, and in magmatic and hydrothermal environments is not completely manifest, and individual occurrences are plausibly explained by alternate hypotheses. In most cases, however, the available data support one hypothesis in preference to others, and in this paper the author has attempted to indicate the most probable origins after consideration of the evidence at hand.

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