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DIFFUSION OF COPPER IN NATIVE COPPER-SILVER "HALFBREEDS"

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Native copper occurs in two diverse geologic environments in the Upper Peninsula of Michigan. In the White Pine area of Ontonagon County, both native copper and chalcocite occur in the relatively flat-lying Nonesuch shale of upper Keweenawan age. Chalcocite is by far the most abundant copper mineral.

Many miles northeast of White Pine native copper deposits are found principally in amygdaloids and conglomerates of lower Keweenawan age. Here the beds dip between 35 and 70 degrees and carry copper that is almost entirely in the native state. Occasionally chalcocite has been observed, but this type of occurrence is unusual.

Most geologists agree that the amygdaloidal and conglomerate deposits are epigenetic, but there is a great deal of controversy regarding the origin of the White Pine deposit. One opinion (Sales, 1959; Joralemon, 1959) has held that this deposit was formed by an epigenetic process involving hydrothermal solutions of magmatic origin. Another theory (White and Wright, 1954; White, 1960) postulates that the deposit was formed by a syngenetic process, involving co-precipitation of copper minerals, silt and organic matter in a delta system.

Most recently, Barghoorn, Meinschein, and Schopf (1965) have reported the results of porphyrin extractions from siltstone of the White Pine Nonesuch shale and analyses of petroleum from the same deposit. They also reported unpublished radiogenic age determinations of the Nonesuch formation by Chaudhuri and Faure which indicate that the formation is 1046 ± 46 million years old. The existence of porphyrins in the siltstone is indicative of a mild thermal history of the deposit. From the activation energy for the thermal breakdown of porphyrins, Barghoorn *et al.* (1965) calculated that the deposit could not have been at 250°C for more than about 100 years, at 300°C for more than about 11.5 days, and at 500°C for more than about 100 seconds. From this evidence, any theory of emplacement of copper minerals that involves sustained high temperature seems quite unlikely.

The object of this note is to present independent evidence which supports the contention (White and Wright, 1954; White, 1960; Barghoorn *et al*, 1965) that the copper minerals were laid down at a low temperature, and have had a mild thermal history since that time. Since other evidence (Butler and Burbank, 1929) strongly suggests that the amygdaloidal and conglomerate deposits are epigenetic, the following discussion is not meant to imply that the Seneca deposit is syngenetic in origin, as may be the case of White Pine, but rather to add supporting evidence that the Seneca deposit was formed by relatively low-temperature solutions.

Silver occurs in small quantities throughout the Upper Peninsula copper deposits, often in the form of native metal intimately associated with copper. In view of the age of the deposit, these "halfbreed" nuggets may well be the world's oldest metallic diffusion couples. In principle, therefore, it should be possible to learn something of the thermal history of these couples by examining interdiffusion across an interface.

Two types of "halfbreeds" were studied. The first was the type usually found in the White Pine deposit, a thin sheet of roughly rectangular form, about 7.5 by 10 cm, and about 0.05 mm. thick, at the most. The silver appeared in the form of small irregular islands, about 3.0 mm. in maximum dimension, but seldom penetrating entirely through the sheet of copper. The second type of halfbreed was the massive kind found in the Kearsarge amygdaloid of the Seneca Mine of the Calumet and Hecla Copper Co., at the 4000- to 5000-foot depth level. Typically, these measured about $7\times3\times1.5$ cm. The silver was present in the copper as isolated masses, with dimensions of about $2\times1\times0.5$ cm.

To prepare the specimens for electron microprobe analysis, they were sectioned, mounted in a small clamp, and given a metallographic polish. Care was taken to ensure that the copper-silver interface was normal to the plane of polish. A reasonably planar section of the interface was selected for the microprobe traverse. To provide a blank specimen with no interdiffusion, a sheet of 99.99 percent Ag, 1.0 mm. thick, was electroplated on both sides with copper, to a thickness of 2.0 mm.

The appearance of an Ag-Cu interface in the leaf specimen from White Pine is illustrated in Figure 1. The dark path marking the microprobe trace is due to hydrocarbon contamination of the surface and is not representative of the microprobe spot size. An interface in one of the more massive specimens from the Seneca Mine is shown in Figure 2.

A Cambridge Instruments electron microprobe was used to determine the distribution of copper in the silver near the interface in the two types of halfbreeds and in the blank. Unfortunately, the high atomic number of silver leads to a quite high level of white X-ray production,

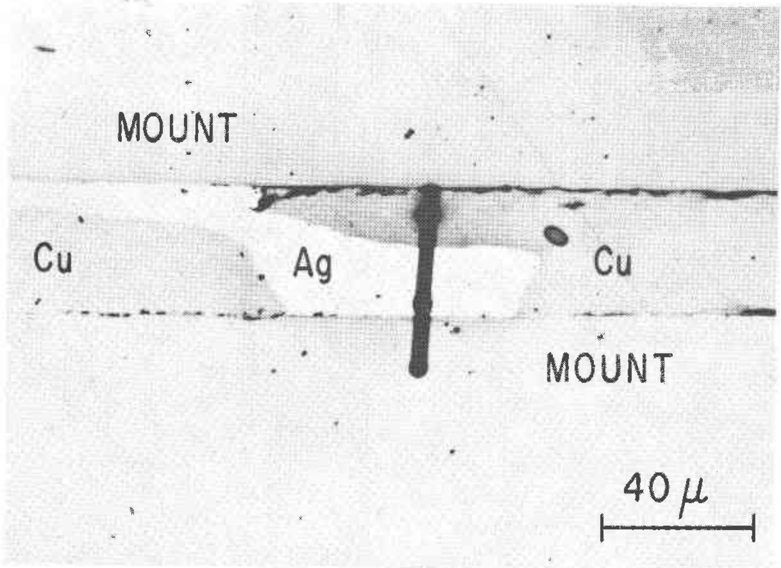

FIG. 1. Section of leaf-type halfbreed, showing electron microprobe trace. White Pine Mine, White Pine Copper Co. As polished.

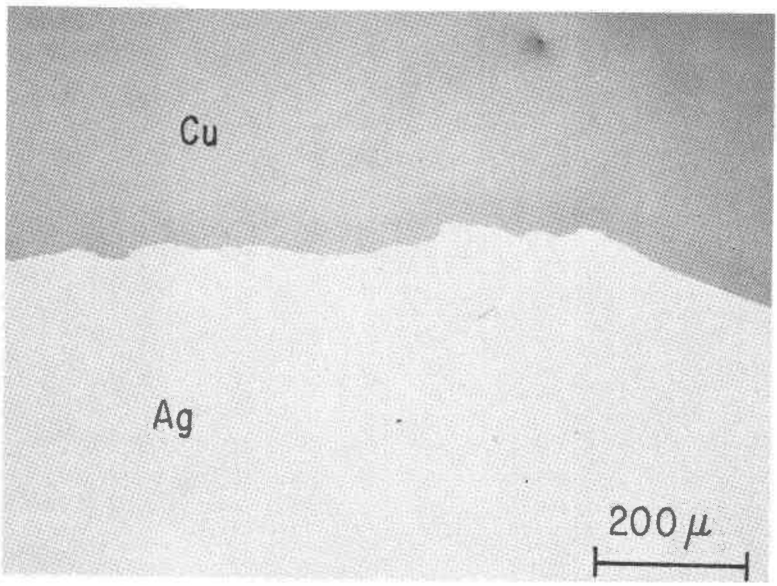

FIG. 2. Section of massive halfbreed from Seneca Mine, Calumet and Hecla Copper Co. As polished.

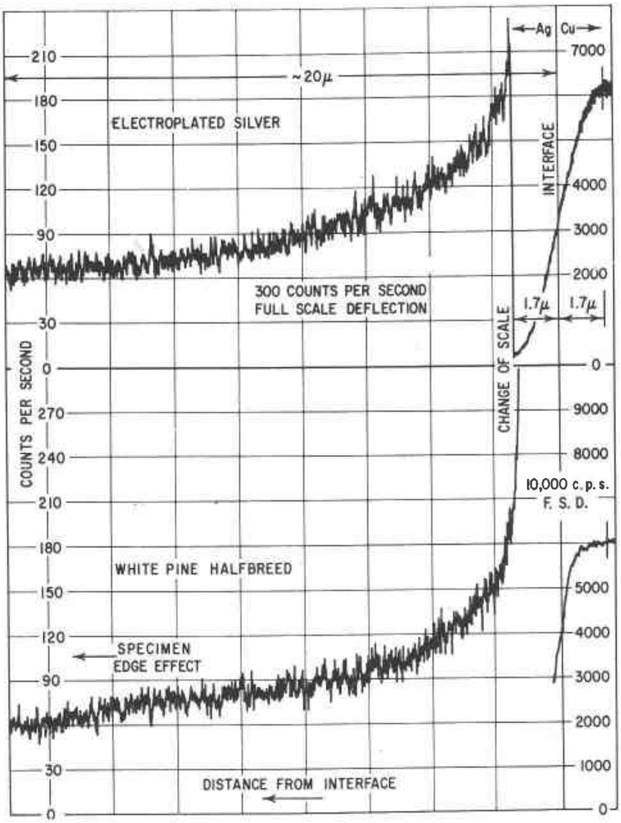

FIG. 3. Electron microprobe traces from a blank specimen with no diffusion of copper into silver, and from a leaf-type halfbreed.

and at the low concentrations of copper involved in the measurements (generally <1.0 percent) a relatively large proportion of the measured copper X-ray intensity is fluorescence radiation, produced by absorption by the copper of the white X rays rather than by direct electron excitation. This reduces the spatial resolution of the analysis, although the effect can be largely overcome by the use of the blank specimen. The detection limit for Cu in Ag was found to be about 0.14 percent.

The apparent copper concentration profile from the blank was subtracted from the profiles obtained from the halfbreeds. As can be seen in Figure 3, the profiles from the blank and from the White Pine specimens coincided, indicating no diffusion of copper into the silver, within the limits of resolution. The boundary is located where 50 percent of the maximum copper count rate was obtained, and within about 2μ of this boundary the existence of any interdiffusion cannot be assessed, despite use of the blank specimen. Assuming, therefore, that copper has diffused to a depth of 2μ in the White Pine halfbreed, some reasonable maxima of temperatures and time can be estimated. There seem to be no available measurements of the interdiffusion coefficient of copper and silver, but the tracer diffusion coefficient of copper in silver has been measured (Sawatzky and Jaumot, 1957). Since the copper content of the silver phase in the halfbreed is very low, <0.15 percent, this tracer coefficient can be used as a good approximation to describe diffusion of copper in the silver phase.

Sawatzky and Jaumot (1957) used the equation

$$D = 1.23 \exp\left(-\frac{46,100}{RT}\right)$$

to describe the diffusion data over the temperature range from 716 to 945°C. Extrapolation of this data to lower temperatures is not a very satisfactory procedure, but it is the only one open to us. Experience indicates that values of D at low temperatures will usually be larger than those predicted by extrapolation of high temperature data. The time, t, required for a penetration, d, of 2μ, the maximum possible in the White Pine halfbreed, can be calculated from the relation

$$t \approx \frac{d^2}{D}$$

with the following results:

Temperature, °C	900	700	500	300
Time for penetration of 2μ	15 sec	15 min	4 days	500 years

These are conservative maxima, and the true figures are almost certainly lower.

The microprobe traces from the Seneca specimens indicated a slight but definite penetration of copper, to a maximum depth of 10μ. The upper limits for time at temperature would then be:

Temperature, °C	900	700	500	300
Time for penetration of 2μ	7 min	6 hrs	100 days	13,000 years

In addition, the complete absence of any eutectic structures, or spheroidized eutectic structures in these specimens indicates that they were never heated to temperatures above about 780°C (Hansen, 1958).

These calculations have ignored any possible effect of pressure on diffusion, but such effects can be estimated. The maximum vertical displacement of the Keweenaw fault, from geophysical evidence, is about

10,000 to 12,000 feet. Consideration of erosion would set the initial vertical displacement at a maximum of about 20,000 feet (Bacon, 1960). Assuming, therefore, a maximum pressure of 20,000 psi and an activation volume of 10.3 cm^3/mole for the diffusion of Cu in Ag (which is probably high by a factor of 2), we calculate that at 300°C the ratio $D_{\text{atm. p.}}/D_{20,000\text{ psi}}$ is only 1.35.

It reasonably may be asked whether diffusion gradients in these copper-silver couples could be removed by extremely slow cooling from an elevated temperature. Given the different particle sizes in the two types of halfbreeds examined, and the diffusivity of copper in silver, it can be shown that equilibration would require periods longer than the history of the deposit at a temperature between 300 and 400°C for the Seneca halfbreed, and at a temperature between 200 and 300°C for the White Pine halfbreed. The solid solubility of copper in silver is 0.7 wt pct at 400°C, 0.4 percent at 300°C, and 0.2 percent at 200°C (Hansen, 1958). These concentrations are above those detected within the silver of the halfbreeds, in areas removed from the Ag-Cu interface. Also, the form of the concentration-distance curve in the Seneca halfbreed indicates that diffusion of copper in silver was away from the interface, which is inconsistent with an approach to equilibrium from a high temperature.

Another indication of a mild thermal history is that native copper is often in a cold-worked state when taken from the rock, because of deformation during rock movement; it is rarely found in the recrystallized condition (Smith, 1965). Recrystallization occurs at about 200°C after 75 percent reduction by rolling and at about 400°C after 25 percent reduction (Schroeder and Clapp, to be published).

From these data, it is obvious that both deposits have had a very mild thermal history, which is the conclusion reached independently by Barghoorn *et al.* (1965) for the Nonesuch ore. We must conclude that the copper and silver in these deposits were reduced and deposited by low-temperature processes, although these processes may differ between the White Pine and the amygdaloid deposits.

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