

15. NATIVE COPPER IN DSDP LEG 40 SEDIMENTS

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ABSTRACT

Native copper makes up 12% (by weight) of a Miocene nanno-fossil ooze at DSDP Site 364, Angola Basin. Copper occurs as botryoidal masses up to 4 mm across and as casts filling planktonic foraminifers, thus proving a syngenetic origin.

Possible sources of the copper are (1) a deep-seated magma, (2) seawater plankton, (3) a sabkha, or (4) a submarine basaltic extrusion (part of the Miocene Cameroon Volcanic Zone?). The last source is tentatively favored. Leaching of this basalt by hot seawater would form a cupriferous Na-Ca-Cl brine which could be transported southward to Site 364 by bottom currents. Organic matter, perhaps aided by bacteria, could act as a precipitant for the native copper.

INTRODUCTION

"Ex Africa Semper Aliquid Novi"

Pliny: *Historia Naturalis*

While examining Leg 40 samples for iron sulfides (Siesser, this volume), the writer found native copper in one of the samples (364-5-2, 19-21 cm). The botryoidal form of most of the copper grains initially suggested in situ formation; subsequent discovery of copper casts of planktonic foraminifers removed any lingering thoughts of contamination.

Site 364 was drilled off Angola in a water depth of 2449 meters (Figure 1). The copper lies in moderate yellowish-brown (10YR 5/4) to light olive-gray (5Y 5/3) Miocene marly nannofossil ooze at a subbottom depth of about 152 meters. Native copper was found in only the sample mentioned, although all other samples at the writer's disposal from this site (364) and the adjacent site (365) were carefully re-examined.

This is not the first report of native copper in DSDP cores. However, all other occurrences have been found in basement rocks (e.g., Site 282) or in sediments immediately overlying basement rocks (e.g., Site 105), from where the copper was presumably derived. Conversely, this copper occurs at least 3 km above volcanic basement rocks, and no copper has yet been found in samples above or below it.

The purpose of this study is (1) to document and describe the first occurrence of nonbasement-associated native copper in DSDP sediments, and (2) to comment on various possible origins for the metal.

PETROGRAPHY

Native copper makes up 12% (by weight) of the total sample in which it was found. The copper grains are reddish-brown, mostly botryoidal masses (Figure 2) and individually range up to 4 mm across. A number of copper casts of planktonic foraminifers are also

present. Color photographs of both the copper masses and foraminiferal casts appear on the frontispiece of this volume. Many of the copper masses are partially coated with very light green calcium carbonate and clay; most, but not all, of this coating is soluble in dilute HCl. The greenish tint is probably caused by reaction of the copper with the surrounding carbonate-rich sediments, forming copper carbonate.

Remaining components of the $>89\mu\text{m}$ size fraction are planktonic foraminifers and a few irregular masses of pyrite. The $<89\mu\text{m}$ size fraction is mostly nannofossils, clay, and zeolites, but also contains a few copper specks.

GEOCHEMISTRY

Electron-microprobe analysis of one copper grain gave the following values for elements other than Cu.

Element	%
K	0.00
Si	0.03
Ca	0.01
Al	0.01
Ti	0.01
Mg	0.01
Fe	0.06
Mn	0.01
S	0.64
Total	0.78%

With the exception of small amounts of Fe and S, the grain can be considered pure copper (the concentrations of the other elements, if real, are negligible). The presence of 0.64% sulfur suggests a very small amount of copper sulfide may be present.

Selected elements in the $<89\mu\text{m}$ size fraction were analyzed by X-ray fluorescence. The following mean values (in ppm) were obtained:

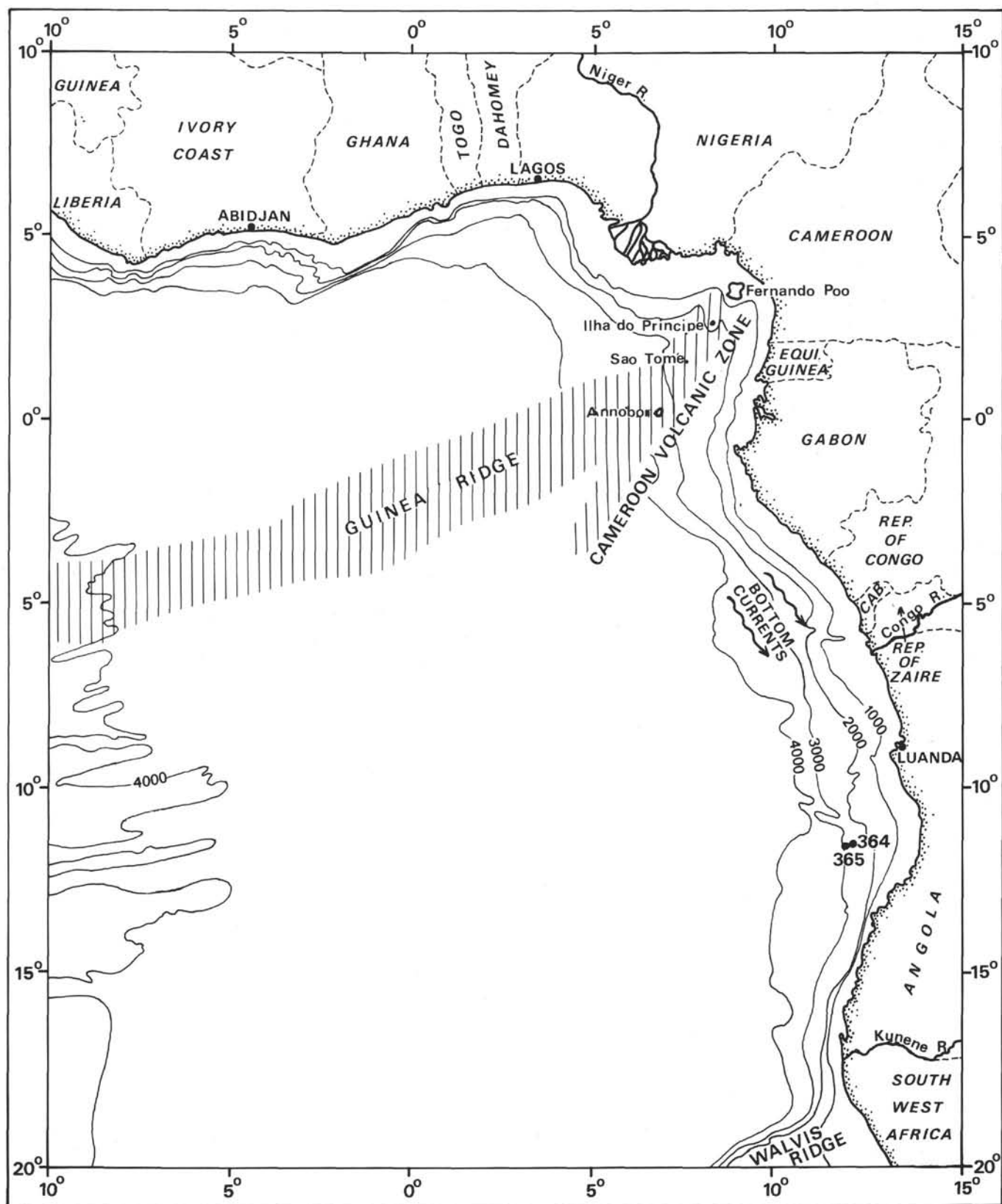


Figure 1. Location map showing Site 364, where native copper has been found, and Site 365. The location of the offshore Cameroon Volcanic Zone is after Emery et al. (1974). Isobaths in meters.

Element	Concentration	Error	Lower Limit of Detection
Cu	3029.38	2.02	1.36
Sr	556.20	1.14	1.70
Zn	204.75	0.54	1.00
Rb	95.46	0.74	1.77
Ni	90.47	0.70	1.67
Zr	74.32	0.68	1.79
Y	20.62	0.56	1.59
Nb	6.92	0.48	1.65

The copper value is obviously vastly higher than in normal marine sediments, indicating that minute copper particles are also present in the fine sediment fraction. Concentrations of the other elements are more or less normal for marine sediments.

ORIGIN

The presence of native copper in any natural environment, whether igneous, metamorphic, or sedimentary, is always somewhat surprising in view of the ease with which copper combines with other elements, especially sulfur. Nevertheless, copper abundantly exists in this form in a diversity of environments. Its presence in sedimentary rocks, the concern of this study, is less common than in igneous rocks, but the literature is still extensive (see Lindgren, 1933, and White, 1968, for useful reviews).

Onshore erosion and mechanical transport of these particles to Site 364 may be discarded as a possible mechanism of origin. It would be difficult to imagine

transport which would bring only copper grains to this site, without other terrigenous grains as well. Moreover, the copper grains are not rounded and abraded, as would be caused by any transporting mechanism capable of carrying these large grains. Finally, the presence of copper-infilled planktonic foraminifers conclusively proves an in situ deposition from cupriferous solutions.

Syngenetic origin of copper in marine sediments requires: (1) a source of the metal, (2) transporting solutions and a force to move them, and (3) a precipitating agent.

Several possible metal sources exist. An underlying magmatic source is unlikely, as it seems doubtful that the ascending cupriferous solutions would not react with other minerals, especially pyrite, forming copper sulfides. The lack of any copper minerals above or below the cupriferous horizon at Site 364 suggests that an underlying magmatic source was not the origin. It might be argued that hydrothermal solutions from an underlying magma are not necessary. For example, connate waters leaching lava beds ascended to deposit native copper in the overlying Nonesuch Shale of Michigan while the mud was still in a semiconsolidated state. The result is a progressive zonation of native copper and copper sulfides in the Nonesuch (White, 1968).

Another possible source for the copper is the seawater itself. Although the copper concentration in seawater is very low, certain phyto- and zooplankton concentrate this, and other, elements in their bodies

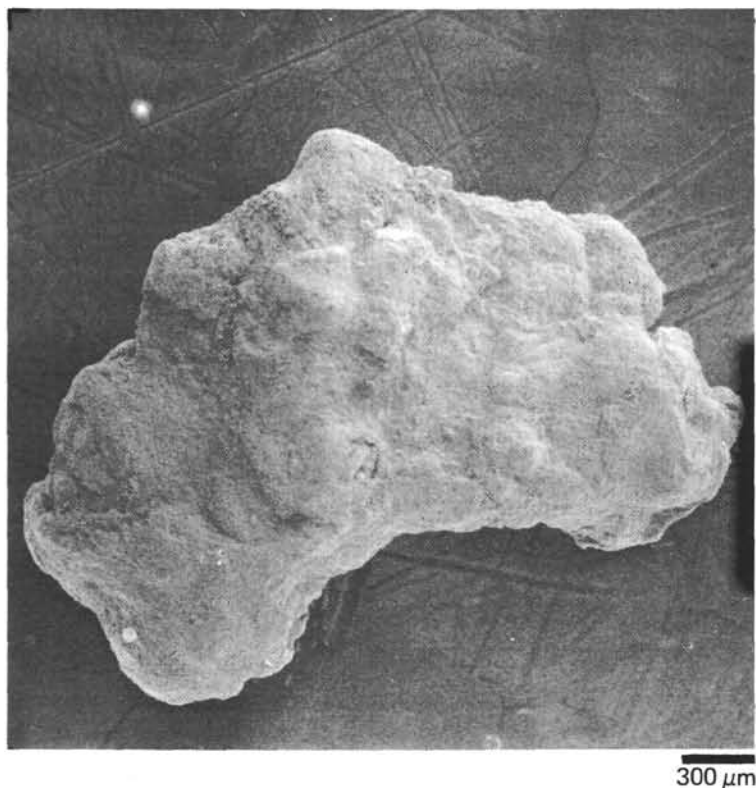


Figure 2. Scanning electron photomicrograph of a grain of native copper. Particles of clay and calcium carbonate adhere to the surface.

(Nicholls et al., 1959; Vinogradova and Koval'skiy, 1962). The plankton die and fall to the sea floor, thus causing localized enrichment of the sediments in those elements. Inshore sediments off southwest Africa, for example, are enriched in copper, lead, nickel, and zinc by this process (Calvert and Price, 1971). In a series of papers, Brongersma-Sanders (1965, 1968, 1969) has stated that the copper-bearing Kupferschiefer Formation of Germany and Poland acquired its metallic content in this manner. Rather specific conditions are necessary for the process: (1) upwelling of nutrient-rich waters, with a concomitant high rate of plankton productivity, and (2) an estuarine-like circulation which would restrict the highest production to the innermost parts of the Kupferschiefer Sea (Brongersma-Sanders, 1965). The decay of vast amounts of dead plankton on the sea floor would exhaust the available oxygen supply, creating an anaerobic bottom environment, with associated production of H_2S . The H_2S would react with plankton-concentrated metals in the sediment to produce Cu, Ag, Pb, and Zn sulfides in the Kupferschiefer (Brongersma-Sanders, 1965).

Several lines of evidence militate against this origin for the Site 364 copper. Upwelling is normally a coastal, rather than an open-ocean (Site 364), phenomenon. Nor is there any sedimentary evidence for upwelling, such as exceptionally abundant diatom or other microplankton remains, fish debris, organic matter, etc. Finally, the characteristic H_2S production which is so necessary for a Kupferschiefer-type origin was obviously not great at Site 364 or copper sulfides, rather than native copper, would predominate.

Renfro (1974) has presented an elegant model to explain strata-bound copper deposits, including the Kupferschiefer, in which the metal source is meteoric water rather than seawater. This model requires a sabkha environment, bordered on its seaward edge by living algal mats. If the sabkha progrades and buries the organic-rich algal mats, favorable conditions are established for the growth of anaerobic bacteria and production of H_2S . Terrestrial waters eventually ascend through the reducing, H_2S -rich environment generated by burial of the algal mat. If the terrestrial waters contain dissolved metals, they will react with the H_2S and be precipitated interstitially as sulfides. Two major points argue against Renfro's hypothesis with respect to the Site 364 copper: (1) the required environment is the coastal region of a shallow marine lagoon or inland sea, whereas the Miocene at Site 364 was a time of open ocean sedimentation and (2) the sabkha environment apparently only produces sulfides, whereas native copper exists at this site.

A fourth possible copper source is cupriferous solutions derived from a submarine basaltic extrusion at some distance from Site 364. This type of source has been described as "volcanic emanations" or hydrothermal exhalations" by many authors. Corliss (1971) has presented geochemical evidence which suggests a model for the origin of submarine hydrothermal solutions. The margins of hot, submarine-erupted basaltic rocks are quickly cooled, forming pillow structures. The chemistry of the pillows approximates

the chemistry of the erupted liquid. The slowly cooled interiors of the flows are, on the other hand, depleted in certain elements which are enriched in pelagic sediments and manganese nodules (Corliss, 1971). This depletion is caused by seawater entering the eruptive flow through contraction fractures, being heated, and dissolving volatiles and metals concentrated in the residual phases within the interior of the extrusion. Corliss further proposes that the metals are mobilized as chloride complexes. This is in accord with the work of White (1968), showing that a Na-Ca-Cl brine is a potent solvent for copper and other metals.

This heavy, metal-enriched brine could move over the sea floor as a gravity flow, bottom currents, or both. It is tempting to consider the northeast-southwest trending Cameroon Volcanic Zone as the possible extrusive source. This volcanic zone extends almost 1100 km offshore, the terminal end being less than 1200 km north of Site 364 (Figure 1). Moreover, the offshore segment is known to have extruded basalt during the Miocene (Baker, 1973). Present-day movement of bottom currents in the eastern Angola Basin is in a southern direction (Shannon, 1970). If a similar circulation prevailed during the Miocene—and Hay (1974) believes that Neogene current patterns were similar to those of today—transport of the brine to the Site 364 area would have been the result.

No matter where the cupriferous brine came from or how it eventually reached Site 364, some agency must have caused it to precipitate native copper. Precipitants that have been suggested to accomplish this are: (1) organic matter (Lovering, 1927; White, 1968), and (2) calcite, prehnite, or zeolites, in association with chloride solutions (Cornwall, 1956).

There have been several reports of native copper forming in modern organic-rich peat swamps (e.g., Forrester, 1942; Eckel, 1949; Lovering, 1927). This is especially intriguing, in view of the occurrence of authigenic marcasite at this site (see Siesser, this volume). Marcasite is a mineral normally associated with peat swamps and is unusual in the marine environment. Its sporadic occurrence at Site 364 suggests periodic conditions of extreme acidity. Bacteria may assist organic matter to precipitate native copper in acidic swamps. Lovering (1927) was able to produce metallic copper experimentally from copper solutions by using swamp bacteria. Apparently the native copper formed by the reaction of bacterial waste products with the cupriferous solutions.

Cornwall (1956) has reported studies in which native copper was precipitated from chloride solutions in the presence of calcite, prehnite, or zeolites. However, it appears that temperatures of 200°-250°C are necessary for this reaction. The high temperature would thus seem to preclude this association as a precipitant at Site 364. However, all of the Miocene cores at Site 364 are zeolite rich (up to 5% of the total sediment) and calcite is ubiquitous.

A concentration of organic matter is thus most likely to have been the precipitant at Site 364, even though the sediments are not enriched in organic matter today. Many questions still remain unanswered. Why, for

example, are no other metals or their sulfides (other than pyrite) found at this horizon? Surely hot brine would have dissolved other metals from the basalt source. Perhaps the fact that the common metals precipitate (as sulfides) in the order Cu, Zn, Pb, Ag may be relevant. Could copper have been precipitated here and then the brine moved elsewhere to deposit other metals?

CONCLUSIONS

The foregoing discussion of the origin of this copper is highly speculative. It is hoped that the hypothesis presented will stimulate further ideas on the genesis of this unusual copper deposit.

Twelve percent native copper in a soft, semiconsolidated carbonate sediment would normally be an economically attractive prospect, especially if, as is likely, the deposit has some lateral extent and is not solely a localized feature. The deposit could have been a Miocene sea-floor feature hundreds of miles in extent, conceivably extending from its hypothetical source (the Cameroon Volcanic Zone?) as far afield as the brine and/or its metal content survived.

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