# 21. NATIVE COPPER IN ODP SITE 642 THOLEIITES<sup>1, 3</sup>

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#### ABSTRACT

Native Cu occurs in amygdules, fractures and groundmass of tholeiites from Ocean Drilling Program Site 642 on the Vøring Plateau. Similar occurrences have been reported in other tholeiites of the early Tertiary North Atlantic Volcanic Province drilled at Deep Sea Drilling Project Sites 342 on the Vøring Plateau and 553 on the Rockall Plateau. The flows containing the native Cu have distinctive alteration patterns characterized by the combination of reddened flow tops, distinctive pastel coloration of the upper parts of the flows, relative abundance of celadonite, and the presence of native Cu. These associations suggest that subaerial weathering and subsequent seawater-basalt interaction are related to the occurrence of native Cu. An additional factor may be the increase in compatibility of Cu in silicates and Fe- Ti oxides that may accompany sub-solidus oxidation of basaltic flows.

Native Cu occurrences in Site 642 tholeiites have some striking similarities to the large native Cu deposits in the Precambrian basalts of the Keweenaw Peninsula, Michigan, that are suggestive of similar mineralization processes.

## **INTRODUCTION**

Concentrations of native copper are commonly associated with rift tholeiites (e.g., Sawkins, 1982), although background Cu concentrations in mineralized rift basalts are often no higher than other basalts (e.g., Jolly, 1974; Basaltic Volcanism Study Project (BVSP), 1981). The ways in which native Cu is concentrated have been the source of some controversy. Subaerial eruption has been recognized, on the basis of empirical observation, to play some role in the concentration of native Cu (e.g., BVSP, 1981, p. 385), although the oxidizing environment would seem to be unfavorable and a concentration mechanism has never been proposed.

In recent studies, subaerial eruption has been downplayed as a factor in native Cu concentration. Recent suggestions for the origin of the large native Cu deposits in the approximately 1200-Ma Keweenawan basalts (northern Michigan and adjacent Ontario) include opposing mechanisms: mobilization of Cu during prehnite-pumpellyite grade metamorphism (White, 1968; Jolly, 1974; Livnat et al., 1983) and high-temperature processes associated with a hidden intrusion (Richards and Spooner, 1985, 1986). Redistribution of Cu at low metamorphic grades seems to be the most popular current model for the concentration of native Cu in ancient tholeiites (e.g., Lincoln, 1981; Sood et al., 1986).

This paper is a preliminary report on native Cu mineralization found in foundered, subaerially erupted tholeiites of the early Tertiary volcanic province of the North Atlantic region (Fig. 1). These occurrences of native Cu in relatively unaltered basalts are, in many ways, strikingly similar to the Precambrian Keweenaw Cu deposits.

#### NATIVE CU IN DSDP AND ODP BASALTS

Native Cu has been reported from seven Deep Sea Drilling Project (DSDP) and Ocean Drilling Project (ODP) sites. Of these, two occurrences are in sediments far above basement (Siesser, 1978; Knox, 1985), another is a native Cu-bearing vein in sediments just above basaltic basement (Scientific Party, 1972), and four are within basalts. One of the reported native Cu occurrences in basalt was in a thoroughly altered chunk of igneous rock recovered from the base of a hole drilled during Leg 29 (Overshine et al., 1975) and is of no further concern to this paper.

The other three basaltic occurrences of native Cu are in North Atlantic Volcanic Province basalts, the early Tertiary (approx. 55 Ma) outpouring of tholeiitic basalt that accompanied the initiation of rifting in the Norwegian-Greenland Sea. Native Cu was reported from Hole 342 on the Vøring Plateau (noted in the barrel sheets, Scientific Party, 1976: core 8, sections 2, 3, and 4). Hole 553A on the Rockall Plateau (Scientific Party, 1984, p. 62), and Hole 642E (Figs. 2 and 3; Table 1).

Native Cu-bearing flows at Site 642 have visibly distinctive and regular characteristics that led to the shipboard definition of "Cu-type" as a subset of fine-grained tholeiitic flows of the upper series (Shipboard Scientific Party, 1987). These characteristics are related to alteration patterns rather than primary flow morphology, although "Cu-type" characteristics were never observed in medium-grained flows in the section. Analyses of little-altered samples from the interiors of individual flows at Site 642 (Viereck et al., this volume) indicate that "Cu-type" flows have background Cu concentrations indistinguishable from units that do not contain native Cu (Fig. 4A).

The secondary assemblage in non-Cu-bearing flows consists of early smectite-replacing mesostasis and filling voids, along with sporadic late calcite and celadonite. Cu-type flows have distinct secondary features:

1. "Cu-type" characteristics are only found in fine-grained flows with reddened tops, but never in medium-grained flows, reddened or not (see Shipboard Scientific Party, 1987).

2. An easily identifiable pink to pinkish-gray coloration persists from the top to near the massive centers of flows.

3. Vesicles, especially near flow tops, are lined to completely filled with vibrant blue-green celadonite that is intimately intergrown with calcite.

4. Native Cu occurs in voids and fractures and, less commonly and in smaller blebs, in the groundmass of massive flow interiors (Fig. 3).

<sup>&</sup>lt;sup>1</sup> Eldholm, O., Thiede, J., Taylor, E., et al., 1989. Proc. ODP, Sci. Results, 104: College Station, TX (Ocean Drilling Program). <sup>2</sup> Lamont-Doherty Geological Observatory, Columbia University, Palisades,

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Cu-bearing flows at Sites 342 and 553 seem to have these same characteristics.



Figure 1. Index map of the North Atlantic region showing the locations of DSDP Sites 342 and 553 and ODP Site 642. The map is from Mutter et al. (1988), to which the reader is referred for full discussion of the features shown.

The reddening of flow tops is believed to have been caused by subaerial weathering during a relatively brief period of exposure before the emplacement of superjacent flows. This interpretation is consistent with the increased intensity of reddening toward flow tops and with the intermittent occurrence of reddened flows. Subaerial weathering is also consistent with the lack of reddening in all but the topmost flows in medium-grained sequences (medium-grained flows are believed to be more proximal, compound flows, erupted in rapid succession), and with the preponderance of reddened flows that are directly overlain by a layer of sediment. Finally, if the reddening of flows were due to a process such as deuteric alteration or interaction with seawater, one would expect most, if not all, flows to be somewhat reddened.

The cause of the pastel coloration in "Cu-type" flow tops has not been identified with any certainty, but the effect is present only in flows containing native Cu. It may in part be due to oxidation and hydration of Fe-Ti oxides and in part to later interaction with seawater. The discoloration might be described as bleaching, but the pastels of the "Cu-type" flows are, although distinctive, not nearly as dramatic as the white to light gray bleaching observed in the lower 50 m of the upper volcanic series and in the lower volcanic series at Site 642 (Fig. 2; Shipboard Scientific Party, 1987).

Celadonite occurs sparingly in all but "Cu-type" flows, in which it is relatively common and brightly colored. Generally, celadonite is confined to the upper, pastel-colored portions of flows, where it occurs as vesicle and fracture fillings. Paragenetic and geochemical relationships suggest that celadonite + calcite formed at the expense of earlier smectite. Celadonites appear to have precipitated at higher water/rock than smectites, and may have formed during two discrete intervals of seawaterbasalt interaction (see LeHuray and Johnson, this volume).

The largest grains of native Cu are about 1 cm in their long dimension and occur in fracture fillings. Native Cu in vesicles may be up to 0.5 cm across. In the groundmass, the largest na-



Figure 2. Lithostratigraphy, chemical stratigraphy, petrography, and alteration synthesis of the volcanic sequence, Site 642. Flows: no ornament = fine-grained flows, right-slant hatching = medium-grained flows, left-slant hatching = mixed flows. Flow thickness: open circles = fine-grained flows, filled circles = medium-grained flows, crosses = mixed flows, triangles = lower series flows, D = dykes. Flow top: G = gray, R = reddened. Dinoflagellate/palynomorph index: N = neritic, P = paralic, E = esturine, A = subaerial. Phenocryst content: S = sparsely phyric, M = moderately phyric, cross-hatching = phyric. Alteration zones: no ornament = low-temperature mineral replacement, right-slant hatching = weathered zone, left-slant hatching = zeolitic and mineralized zone. This figure is from Shipboard Scientific Party (1987).

tive Cu grains are just visible to the naked eye, but seem to occur in flocks, so that occassionally they make up several tenths of a percent of groundmass volume.

A simple, three-step model for native Cu concentration can explain the observed features of "Cu-type flows" at Site 642:

1. Cu that is not lost, along with sulfur, to the vapor phase is concentrated in opaque oxides and pyroxenes;

2. Cu is released during oxidation of Fe-Ti oxides to hematite during subaerial weathering;

3. Seawater reacts with basalts to (a) mobilize and (b) concentrate native Cu:

3a. When seawater is introduced, seawater-basalt interactions result in Cu mobilization and adsorption(?) onto smectites; and 3b. Later, smectite reacts further with seawater to form celadonite under conditions favorable to native Cu formation.

Absorption of heavy metals onto alteration phases has been suggested to occur based on experimental evidence (Seyfried and Janecky, 1985).

Late stage celadonite precipitation in basalts has been associated with "oxidative" conditions (e.g., Bass, 1976; Scheidegger and Stakes, 1977; Stakes and Scheidegger, 1981), which would seem to be unfavorable for the precipitation of native Cu. At Site 642, native Cu is associated with the reaction of smectite and seawater to form the assemblage celadonite + calcite, as discussed in LeHuray and Johnson (this volume):



1mm



### в

Figure 3. Photographs of occurrences of native Cu in F67. (A) Scanning electron microscope images of native Cu (white) in a smectite-filled vesicle (left image shows surface topography, right is a backscatter image in which lighter colors are associated with heavier elements). Sample 104-642E-63R-2, 143-147 cm, cracks in the smectite are due to desiccation. (B) Reflected light image, about 18 mm across, of native Cu in a smectite-filled fracture, section 104-642E-63R-2, piece 1E.

(1)  $2[(0.5 \text{ Ca})(\text{Fe},\text{Al},\text{Mg})_4(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot \text{nH}_20 + 2\text{K}^+] \rightleftharpoons$ (smectite)

$$2[K_2(Fe,A1,Mg)_4(Si,A1)_8O_{20}(OH)_4 + nH_20 + 0.5 Ca^{++}]$$
  
(celadonite)

(2)  $2(0.5 \text{ Ca}^{++} + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + 2\text{H}^+$ .

The excess hydrogen ion produced by reaction (2) could have been the agent of reduction of Cu oxides to native Cu:

$$(3a) 2(0.5 \text{ CuO}) + 2\text{H}^+ = \text{Cu}^\circ + \text{H}_2\text{O}$$

and/or

(3b)  $Cu_2O + 2H^+ = 2Cu^\circ + H_2O$ .

Table 1. Flows with "Cu-type" characteristics at Site 642. Flow numbers as in Shipboard Scientific Party (1987).

Flow no.	Top <sup>a</sup> (core-section, cm)	Bottom <sup>a</sup> (core-section, cm)	Flow thickness <sup>b</sup> (m)
F15	15-5, 122	16-2, 123	4.0
F17	16-3, 100	18-4, 150	18.5
F18	18-5, 0	19-4, 137	7.8
F38	33-1, 138	33-5, 134	6.9
F47	38-4, 0	38-4, 100	3.1
F66	62-1, 17	62-1, 135	2.0
F67	63-1, 0	64-4, 103	10.5
F70	65-1, 0	65-1, 64	3.9
F72	65-1, 112	66-4, 67	11.3

<sup>a</sup> Tops and bottoms of recovered flows. See Shipboard Scientific

Party (1987) for interpolated depths below sea floor. <sup>b</sup> Flow thicknesses are inferred from recovery, drilling records, and well logs.

The absence of precise geochemical formulae for the clay minerals involved in the reactions, as well as uncertainties in the thermodynamic parameters of clavs, make these reactions difficult to evaluate quantitatively. Empirical and Sr isotope evidence, however, suggest that these or highly similar reactions did occur at Site 642.

# THE BEHAVIOR OF CU IN BASALTS, AND A PRELIMINARY EVALUATION OF THE **EMPIRICAL MODEL**

To approach an understanding of why native Cu is concentrated in flows with the "Cu-type" characteristics, it is important to have some information on the distribution of Cu in basalts. Much of the Cu in basaltic rocks has been thought to be concentrated in magnetite (i.e., Fe-Ti oxides) and clinopyroxene, both of which have (effective)  $D_{Cu} \approx 2$  (Eilenberg and Carr, 1981; Jensen, 1982) and into olivine (Scofield, 1976). A minor amount of copper may occur in plagioclase, in which Cu<sup>+1</sup> may substitute for Na<sup>+1</sup> (e.g., Jensen, 1982; Hofmeister and Rossman, 1985.)

Burns and Fyfe (1967) believed that crystal field effects make it unlikely that Cu<sup>+2</sup> subsititutes directly into the spinel structure of magnetite and some authors have stated that copper may instead be adsorbed onto the surface of magnetite (e.g., Scofield, 1976). Jensen (1982), however, found lattice-bound Cu in primary Fe-Ti oxides as well as in pyroxenes and plagioclases, with an apparent correlation between oxidation state (as indicated by Fe-Ti-oxide species present) of the lavas and the amount of lattice-bound Cu. With increasing oxidation state, latticebound Cu also increases; with the appearance of pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>), most of the Cu is lattice-bound, whether in oxides or silicates. In lavas at low oxidation states most Cu is apparently loosely held (Jensen, 1982). The oxidation state of lavas apparently changes rapidly after eruption while the lava is still partially molten (Christie et al., 1986). Magnetite-ilmenite geothermometry of basalts indicate that subsolidus reaction is virtually universal (e.g., Haggerty, 1976). The implications of Jensen's results combined with the findings on oxidation of basalts indicates that the fate of Cu is strongly controlled by posteruptive hot-rock oxidation processes.

The Hole 642E tholeiites totally lack sulfides, as is typical of subaerially erupted basalts (e.g., BVSP, 1981). It seems likely that sulfur, along with some proportion of the Cu, is lost to the vapor phase (e.g., Jolly, 1974). Whether the remaining Cu ends up as an adsorbed or interstitial (loosely held) phase or as a lat-



Figure 4. Frequency distribution diagrams of (A) Cu concentrations in "least -altered" basalts from Site 642 (data from Viereck et al., this volume); and (B) thicknesses of medium-grained, fine-grained, and "Cutype" flows in the ODP Site 642E upper series. The different flow types are discussed in the text and in Shipboard Scientific Party (1987).

tice-bound trace constituent of oxides and silicates would seem to depend on posteruptive oxidation processes. The location of the Cu will strongly affect the ability of seawater or hydrothermal fluids to leach Cu from the basalt.

If Jensen's (1982) results are valid for basalts in general (as far as I know, they have never been independently tested), it seems reasonable to posit that native Cu concentrations are most likely to occur in basalts (a) that have undergone extensive subsolidus oxidation reactions, followed by (b) the breakdown of Fe-Ti oxides to hematite or Fe hydroxides, which is most likely in subaerial environments, and (c) that are then exposed to conditions, such as incursion by seawater or metamorphic fluids, that promote local mobilization and precipitation of the native metal. The first step insures that Cu remains in the basalt rather than being lost with the volatiles at low confining pressures, by increasing the compatibility of Cu in crystallizing phases. The second step makes the Cu available to the fluid phases of the third step.

The implications are that subaerial eruption is indeed conducive to the later formation of native Cu concentrations, because it allows for both extensive subsolidus oxidation of lavas and for release of Cu from lattice-bound sites during hematitization and hydration of opaque oxides. Native Cu may not be concentrated, however, unless a fluid phase is introduced. In the case of Hole 642E tholeiites, the fluid was seawater (LeHuray and Johnson, this volume), but it is conceivable that later metamorphic or magmatic fluids could instigate a similar process of concentrating oxidized Cu from weathered flow tops.

The absence of "Cu-type" characteristics in medium-grained 642E tholeiites, which are thinner than the fine-grained flows

and are believed to have been erupted in quick succession, may be due to some combination of reduced oxidation in more rapidly cooled thin flows and absence of subaerial weathering effects because of rapid burial.

The apparent requirement of an abundant fluid phase may explain the absence of native Cu concentrations in some subaerial tholeiite provinces, such as the Columbia River and Deccan Trap basalts.

# COMPARISON WITH NATIVE CU IN THE KEWEENAW BASALTS

In many respects, the features of the 642E "Cu-type" flows and of Vøring Plateau stratigraphy are similar to characteristics of native Cu deposits of the Keweenawan basalts and of Keweenaw Peninsula stratigraphy. The Keweenawan basalts (Portage Lake Lava Series) are overlain by the Copper Harbor Conglomerate and the Nonesuch Shale, both of Keweenawan age. At Site 642 the tholeiitic section is overlain by an unconsolidated pebble horizon and by marine sediments. Thus, the eruption of both the Keweenaw and Vøring Plateau lavas was followed by a period of erosion and subsidence. As both sections are closely associated with continental rifting events, it is not surprising that their stratigraphy is similar.

Native Cu concentrations occur mainly in fractures and voids in Keweenawan basalts and in interlayered sediments, with small, often microscopic, concentrations in massive flow centers (e.g., White, 1968). In addition, like Site 642 tholeiites, the interiors of Keewenawan flows are remarkably unaltered and the Keweenawan amygdaloidal Cu deposits are largely confined to flow tops that are reddened and to fracture systems cross cutting those flows. Mineralized Keweenaw flows commonly show some bleaching effects near the flow tops. Broderick and Hohl (1935) and Broderick (1935) attributed-and White (1968) and Scofield (1976) apparently accepted-the reddening of flow tops to deuteric alteration, involving volatile transfer from the interiors to the tops of flows, which resulted in oxidation of Fe-Ti oxides and alteration of glass and primary silicates. It seems curious that deuteric oxidation should be concentrated in the tops of Keweenawan flows given the evidence from recent flows in Iceland and Hawaii that deuteric effects are greatest in the interiors of flows, where volatiles are trapped by the cooling flow selvages (Watkins and Haggerty, 1967; Haggerty, 1976).

Amygdaloidal lodes in the Keweenawan basalts are associated with the thickest flows (White, 1968). This has led to the suggestion that Cu mineralization may in some way be related to within-flow differentiation. Cu-type flows at Site 642E, however, have thicknesses that are relatively evenly distributed within the population of fine-grained flows (Fig. 4b).

Scofield's (1976) study of the Keweenawan basalts showed quite clearly that the main source of Cu was the oxidation of primary Fe-Ti oxides, thus supporting previous workers' (e.g., White, 1968; Jolly, 1974) models that the basalts themselves were the source of the Cu. Much of the oxidation, however, appeared to have occurred prior to low-grade metamorphism (Scofield, 1976).

The striking similarities between Hole 642E native Cu-bearing flows and the Keweenawan amygdaloidal lodes suggest that similar processes operated in both the Precambrian and early Tertiary basalts. Both sequences were subaerially erupted, and may therefore have undergone extensive subsolidus oxidation and, according to Jensen's (1982) results, incorporation of Cu into the lattices of crystallizing oxides and silicates. The subaerial environment resulted in weathering and breakdown of Fe-Ti oxides in Site 642 basalts. In light of the finding that deuteric effects are concentrated in flow centers in young basalts, the interpretation of the cause of reddened flow tops in the subaerially erupted Keweenaw basalts should be reevaluated. It seems likely that subaerial weathering effects may be another point of commonality between the Keweenaw and North Atlantic tholeiites.

Most workers agree that native Cu mineralization in the Keweenaw basalts is closely related to low-grade metamorphism, and no evidence for significant seawater-basalt interactions has been reported. Thus, the fluids responsible for concentrating the Cu may have been metamorphic rather than the seawater that operated at Site 642. On the other hand, the Keweenawan basalts foundered during posteruptive subsidence and may have been exposed to high water/rock at that time. The possibility cannot be discounted that early native Cu mineralization in the Keweenaw district, concentrated by the mechanism proposed for Site 642, has been overprinted and obscured by metamorphism, during which Cu was remobilized and further concentrated.

The suggestion has been made that native Cu concentrations in Keweenawan basalts are due to the effects of a hidden intrusion. An intrusion seems too localized a process to explain the aerial extent of mineralization in Upper Michigan and adjacent Ontario. The flow-top weathering release mechanism proposed for Sites 642, 342, and 553, on the other hand, could operate on the scale of the North Atlantic region because Cu would be potentially available from foundered, subaerially erupted basalts at each locality.

#### SUMMARY

Preliminary studies of native Cu mineralization in foundered North Atlantic Volcanic Province tholeiites suggest that three steps were involved in concentrating Cu. The first was subaerial eruption and associated subsolidus oxidation reactions, which apparently increases the compatibility of Cu in crystallizing Fe-Ti oxides and primary silicate minerals. The second step was the release of Cu from Fe-Ti oxides broken down during subaerial weathering. Finally, the incursion of seawater into the porous vesicular flow tops allowed remobilization of Cu and precipitation of the native metal.

The tectonic environment and stratigraphic sequence of Site 642 were essentially the same as those of the late Precambrian Portage Lake lava series of the Keweenaw Peninsula. The characteristics of native Cu mineralization at both sites have many similarities, including association with porous, reddened tops of flows. The Keweenawan basalts have, however, undergone lowgrade metamorphism with the result that the pre-metamorphic alteration mineralogy and Cu distribution patterns are obscured. Despite this complication, the similarities between the Tertiary and Precambrian native Cu-bearing lavas are striking, and suggestive of similar mineralization processes.

Finally, the effects of subsolidus oxidation on Cu compatibility reported by Jensen (1982) seem to agree with the model of native Cu concentration in subaerially erupted basalts proposed here, and may be extremely important to the understanding the sources of Cu in many types of deposits. If oxidation similarly effects the compatibility of other elements, then it could prove important to deconvolving trace-element behavior during hydrothermal alteration and partial melting. Clearly, subsolidus effects demand further investigation.

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