

Life in a Copper Province

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Introduction

The North American Lake Superior region contains a world-class copper province nearly 300,000 km² in area (Fig. 17.1). A dozen major copper deposits and hundreds of smaller mineral accumulations are located in Michigan, Minnesota, and Ontario (Morey and Sims 1996), many of which include As, nickel (Ni), platinum (Pt), palladium (Pd), Co, Mo, and Fe, as well as Cu (Nicholson et al. 1992). Historically, the province has hosted a variety of life forms; fossil biota have been traced as far back as 2.6–2.75 Ga. Palynological and microbial research (Robbins 1985, Robbins et al. 1994) prompts speculation about possible correlations between copper and the biota that evolved there. Because the region has been subjected to continental collisions, volcanism, glaciation, rifting, weathering, sea level rise and fall, waxing and waning of lakes, soil formation, and now to human settlement and development including mining, the fossil record is discontinuous. This review of the geologic formations in the Lake Superior region from the Precambrian to the present, and their copper and biotic occurrences and associations, attempts to illuminate some of those geologic/biologic correlations, and includes mention of modern environmental concerns.

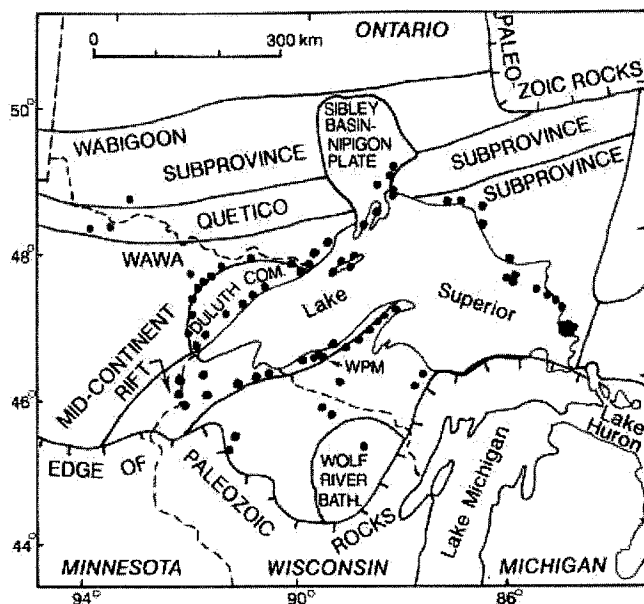


Figure 17.1: Copper deposits and occurrences (from Cannon and McGervey 1991, Chandler et al. 1982, Nicholson et al. 1992, Sims et al. 1993).

Key: • = copper accumulations; bath. = batholith; com. = complex

Biology of Copper Utilization

Copper is one of nearly 75 chemical elements contributing to metabolic or structural functions of organisms (Dexter-Dyer et al. 1984). Bioassimilation varies and depends not only on availability from the environment, but also on the species, gender, and age of organism with specific concentrations also depending on diet, health, tissue assayed, and various synergisms with other trace elements such as Fe and Zn. Indeed, copper is an essential element and co-factor contributing to copper-associated polypeptides that provide catalytic and electron transfer functions in almost every known group of organisms alive today, from bacteria to humans. Copper proteins contribute to skin pigmentation, nerve coverings, and in mechanisms of development, maintenance, and repair of connective tissues important for well-functioning cardiovascular systems (Eisler 2000). Presently, over two dozen essential copper proteins, some with porphyrin-copper functional groups (similar to the porphyrin-iron association in hemoglobin), have been identified, each with its specific developmental or physiological function (Cowan 1998) (Table 17.1).

Adult humans contain between 1.4–2.1 mg Cu/kg of body weight, derived primarily from legumes, potatoes, nuts, seeds, and beef. The new Recommended Daily Allowance for copper for adults in the United States is 900 µg/day, with 10 mg/day the suggested upper limit (NRC 2001). Excess Cu is normally excreted. Copper toxicity, however, has been identified, such as Wilson's Disease, a rare human genetic disorder (Sternlieb 2000) and there are also non-genetic based excesses that may lead to chronic pulmonary disorders, cirrhosis, and may even result in death (Muller et al. 1998). Normally detoxification is through expulsion via cellular copper pumping (Weissman 2000) or metallothionein sequestration, a method that combines the metal with sulfhydryl groups (Fabisaik 1999). Some bacteria can precipitate excess as aqueous forms of copper on their cell walls or membranes (Robbins et al. 1994). The apparent ubiquitous requirements for copper and the ability to avoid its toxic activity suggests copper may have been available, required, and used at the origin of life, and continues to this day as essential in certain roles throughout many if not all life forms (Beck and Ling 1977).

Geologic Abundance and Mobility of Copper

Crustal and sedimentary rocks range in copper concentration from 24–45 mg/kg world-wide, although marine black shales have concentrations up to 300 mg/kg. Estimates of worldwide concentrations of copper vary from 0.2 to 30 µg/L in fresh water and 0.05 to 12 µg/L in seawater (Hem 1985). Pourbaix (1966) showed that the dissolved form of bioavailable copper is cuprous (Cu^+) in dilute waters ($\text{Cu} < 1$ ppm) or anoxic water, cupric (Cu^{++}) in acid or neutral oxygenated waters, HCuO_2^- in oxygenated alkaline water ($\text{pH} > 8.5$), and CuCl_2^- , when water contains NaCl. Concentrations of total dissolved copper in Lake Superior ($\text{pH} 8$) ranged from 1.4 to 6.9 µg/L between 1970 and 1973 (Weiler 1978). Soils from Cambrian sandstones in the Pictured Rocks Lakeshore area, MI, have assayed 150 ppm (Schacklette 1967).

Linkages: Geological and Biological Processes

Major compilations of the geology of the Lake Superior region (Sims and Carter 1996), and distribution of copper through time (Jacobsen 1975) are available (Table 17.2). This chapter focuses instead on those rocks that couple copper with carbon or fossil materials, although 66% of stony meteorites bear native Cu Rubin (1994). The region is known also for its world-class Precambrian iron-formation deposits (LaBerge 1994), which may contain copper (Kirkham 1979). However, the important copper minerals in this region are native copper (Cu^0), chalcopyrite (CuFeS_2), chalcocite (Cu_2S), bornite (Cu_5S_4), domeykite (Cu_3As), and malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$).

As an organism enters the fossil record, its metal components accompany it to deposition (Honjo et al. 1982). Interpreting relationships between fossil organisms and metals enclosed within their tissues relies on a variety of microtechniques, including palynological analysis using light microscopy, scanning electron microscopy (SEM), and isotopic analysis. Black opaque copper sulfide mineral(s) were identified enmeshed in organic tissue fragments of the Proterozoic Nonesuch Shale in the region (Robbins 1983, Robbins and Traverse 1980). Similarly, Sillitoe et al. (1996) identified bacterial clusters with chalcocite that formed at the replacement fronts with chalcopyrite or pyrite in a Chilean copper deposit.

Table 17.1: Copper proteins. The table lists identified copper proteins and their functions within taxonomic categories (adapted from Cowen 1998 and Margulis and Schwartz 1998). Copper proteins require at least one copper ion or copper as a cofactor for metabolic activity. (X= Known user; ? = Possibly used; na = Information not available)

Function	Protein Names	Bacteria	Protoctista	Animalia	Fungi	Plantae	
Catalysis	Amine oxidase	X	na	X	X	X	
	Ammonia monooxygenase	Nitrifying bacteria	?				
	Ascorbate oxidase					Fruits and vegetables	
	Ceruloplasmin			Mammals			
	Cu,Zn SOD ^(a)	X	na	X			
	Cytochrome c oxidase	Aerobic bacteria	X	X	X	X	
	ba(3) and caa(3) ^(b)	X					
	Diamine oxidase	na	na	X	na	X	
	Dopamine B-hydroxylase	na	na	X			
	Glactose oxidase			Mammals			
	Laccase				X	X	
	Lysl oxidase			X			
	CH ₄ monooxygenase	X	?				
	N ₂ O reductase	X					
	Nitrite reductase	X					
	Peptidylglycine hydroxylating monooxygenase				X		
	Tyrosinase				X	X	X
	Ubiquinone oxidase	X	X	X	X	X	X
	Electron transfer	Auracyanin	Chloroflexus ^(c)				
		Azurin	X	na	na	na	X
Phytocyanin family						X	
Plastocyanin family		Cyano-bacterium ^(d)	Green algae			X	
Rusticyanin		X					
Metallothioneins	Cu-MTN	na	na	Drosophila	X	na	

(a) Cu,Zn superoxide dismutase

(c) Chloroflexus aurantiacus, green gliding primitive photosynthetic bacterium

(b) Members of the Cytochrome C oxidase group (d) Prochlorothrix hollandica

Isotopic variations (as δCu^{65} in parts per thousand, ‰) can provide some evidence of biological fractionation. In the Lake Superior province, fractionation has been measured on native copper (-1.8 ‰), on chalcocite and on domeykite (0.0 to +1.4 ‰), and in host rock shales/siltstones/sandstones (-3.6 to +1.4 ‰) (Shields et al. 1965, Walker et al. 1958). Although multiple physical sources of copper exist, Zhu et al. (2000) interpret the isotopic variability as biological fractionation at low temperatures.

Within the large Lake Superior region, the earliest organic carbon appears in the Late Archaean (2.6–2.75 Ga) Soudan Iron-Formation of the Vermilion Range, Wawa Subprovince. The meta-sedimentary marine rocks were found to contain bacteria or cyanobacteria (Cloud et al. 1965). Micro-techniques have yet to be applied to determine if copper mineralization is directly related to in situ organic carbon layers. In the Wabigoon Subprovince, the Ontario Atikokan area has chalcopyrite (Kirkham 1979) and spectacular domed dolomitic stromatolites created by sediment-coated cyanobacteria, possibly assisted by other bacterial species (Wilks and Nisbet 1985). Pyrite with biogenic sulfur values occurs in horizons above these stromatolites (Strauss 1986).

The Middle Proterozoic (1.0–1.6 Ga) contains fossilized algal filaments and pellet-shaped microfossils that may be the earliest organic remains in the Marquette Range of Michigan. Copper sulfide mineralization (Clark 1974, Mudrey and Kalliokowski 1993) is associated with the Kona, Negaunee, and Michigamme Formations that have organic carbon as microbial remains, stromatolites, and algal filaments (Cloud and Morrison 1980, Han and Runnegar 1992). In the Animikie Basin of Minnesota and Ontario, the Rove Formation in the Gunflint Range shows copper mineralization (Reed 1967) and microfossils of bacteria, pellet-shaped structures that may represent the oldest fecal pellets of simple multicellular animals (Robbins et al. 1985), and worms (Edhorn 1973).

The tectonic activity of the Late Proterozoic (0.6–1.0 Ga) (Cannon 1992) resulted in many copper deposits along with high biological productivity in a rift valley lake (Daniels 1982). The black shale of the None-

such Formation lakebeds contains petroleum, and fossil cyanobacterial sheaths, fungal hyphae-sized tissues, and aquatic algae (Robbins 1983). The variety of pellet-shaped microfossils and spore triads (Strother 1986) implies that microscopic animals may have lived and reproduced in the water column (Robbins et al. 1985). Chalcocite enmeshed within organic tissues in the shale (Robbins 1983) indicates that phytoplankton and/or their microbial degraders may have interacted with copper in the lake water.

The Nonesuch deposits show organic matter had been buried to petroleum-generating temperatures, and Robbins (1985) made the suggestion that catalytic copper metallo-proteins may have entered into petroleum-generating reactions. Copper concentrations in heavy petroleum and bitumen in the region assay 2–4x higher than in surrounding reservoir rocks and sediments (Hosterman et al. 1990), indicating either higher bioaccumulation and/or greater retention of copper depending on local environmental conditions.

Beginning about 2 million years ago, continental glaciers, perhaps 1000 m thick, covered this northern landscape, scraped the land, redeposited boulders containing native copper (Reed, 1991), and removed evidence of any interactions between Pleistocene organisms and copper.

Chalcocite ore, found within the lower beds of the Nonesuch shale, with an average concentration of 1.1% Cu has been mined since the late 1800s until 1995 at the White Pine Mine, Michigan (White and Wright 1954). Today brine pools in the White Pine Mine are coated with films of floating blue-green copper minerals and petroleum that drip through roof bolts 820 m underground. The green color of the films is due to the copper chloride minerals, atacamite and para-tacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$], which surround Gram negative bacterial rods and filaments, leading Robbins et al. (1994) to suggest that modern bacteria participate in the mineral formation from mine water that has 7 ppm Cu. These minerals are enriched in C^{13} relative to the local petroleum, which is the likely carbon source. The bacterial role in forming the copper chloride minerals is presently under study.

Table 17.2: Geologic history, copper mineralization, and fossils in the Lake Superior Province

<i>Age (billion years)</i>	<i>Geologic Time</i>	<i>Cu Mineralization</i>	<i>Fossils</i>	<i>References</i>
3.9-4.6	Hadean	Cu in 66% meteorites		Rubin 1994
2.6-2.75	L. Archaean	Chalcopyrite in Atikokan area	Stromatolites with bacteria/cyanobacteria	Morey and Sims 1996; Kirkham 1979
		Native Cu, Soudan Iron Fm	Oldest organic C in Lake Superior range (bacteria?, cyanobacteria?)	Cloud, et al. 1965; Morey and Sims 1996
~1.9-2.1	M. Proterozoic	Carbonate-hosted stratiform Cu mineralization	Organic C and stromatolite fossils; algal filaments	Cloud, et al. 1965; Morey and Sims 1996
1.0-1.2		Volcanic and sedimentary hosted Cu deposits; native Cu along faults	Cyanobacterial sheaths, fungal hyphae-sized tissues, algae, and amorphous organic tissues; pellet-shaped microfossils	Alyanak & Vogel 1974; Cannon 1992; Cannon et al. 1989; Morey and Sims 1996; Nicholson, et al. 1992; Robbins 1983
0-0.6	Cambro-Ordovician	Cu oxide minerals stain cliff faces at Pictured Rocks National Lakeshore	Trilobite, brachiopods, mollusks, trace fossils	Runkel, et al. 1998; Wirth, et al. 1998
0.2	L. Ordovician to M. Devonian	None reported, but Noranda Cu deposit in Quebec of equivalent age	Bivalves, gastropods, conodonts, brachiopods, crinoids	Cannon and Nicholson 2001

Impact of the Last 10,000 Years

Archaic Indians arrived in the region about 10,000 years ago; they dug thousands of copper quarry pits, some several meters deep, on Isle Royale and on the Keweenaw Peninsula. Copper implements, shown to originate from the Lake Superior region by neutron activation analyses, have been found along the east coast of the United States as far south as Florida and even into Mexico (Julig et al. 1992).

Pre-European vegetation in the Lake Superior basin was characterized as a conifer-hardwood forest (Wright 1972). Where copper-bearing rocks weather at the surface, conifers can concentrate copper in tissues (to 700 ppm) and exudates (to 1500 ppm) above background soil (70 ppm) (Curtin et al. 1974). At Pictured Rocks National Lakeshore, Shacklette (1967) measured 1.5 weight % Cu in the ash of the copper-accumulating moss, *Mielichhoferia*, which was growing on a soil derived from a Cambrian sandstone (150 ppm Cu). Studies on phyto-

uptake of copper show that "non-accumulator" terrestrial vegetation has mechanisms for excluding copper, unless the soil is acid (Chaney et al. 2000). Wild rice in non-contaminated lakes in the Lake Superior region naturally concentrates copper in edible seeds (5.3 ppm), in stems (1.4 ppm) and roots (4.8 ppm) (Bennett et al. 2000).

Toxicological studies undertaken in Lake Superior showed elevated copper in fish (Lucas et al. 1970), amphipods (Kraft 1979), mollusks (Kraft and Sypniewski 1981), and oligochaetes (Phipps et al. 1995). The LC_{50} (lethal concentration for 50% of the test group) for fish is less than 1 μg Cu/L, as Cu above this concentration becomes overload and interferes with gill function and acid-base regulation (Tao et al. 2000, Wang et al. 1998). Fish and wild rice are staples of the Ojibwa subsistence populations, and there is the fear that copper accumulations might reach concentrations toxic to these humans (Joseph M. Rose, Sr., personal communication 1993).

Past and present industrial practices add to this concern: copper smelting emissions have been linked to morbidity as well as to respiratory cancers, although metals associated with copper, such as As, Cd, Ni, and Pb, are more usually implicated (Andrzejak et al. 1993, Hwang et al. 1997, Lubin et al. 2000). However, a case study in northern Ontario among Ojibwa-Cree Indians identified 6 children with high hepatic copper concentrations (Phillips et al. 1996).

Conclusions

Copper is readily bioavailable in the Lake Superior region. Though essential for life, elevated concentrations of copper can become toxic. As in the geosphere, biological copper is associated with other metals, such as As, Co, Fe, Mo, Ni, Pd, Pt, and Zn, each with toxicity thresholds and synergisms of their own. Additional concentrations of copper and other metals can be released to the environment from anthropogenic sources including mining, atmospheric deposition, copper plumbing (Eife et al. 1999), and cuprous chloride from road salt. (G.L. LaBerge, oral communication 2001). A major concern is that additional bioavailable concentrations of Cu may increase above toxicity thresholds of the biota living in the area, some of which are the major food staples of indigenous Americans.

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