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Biological geochemistry in the Lake Superior copper province

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The Lake Superior province (LSP) hosts world-class copper deposits; mineralization is wide spread, primarily as native copper (Cu^0), chalcocite (Cu_2S), bornite (Cu_5S_4), chalcopyrite ($CuFeS_2$), and less so as domeykite (Cu_3As) and malachite ($Cu_2(CO_3)(OH)_2$. Copper in A-horizon soils in LSP ranges from 4-1300 ppm, with higher values near known Cu mineralization (6). In contrast, the range for A-horizon soils in the Northern Great Plains is 3-30 ppm Cu (USGS 1977). The LSP has long hosted a variety of life forms; fossil biota have been traced as far back as 2.6-2.75 Ga (2). Palynological and microbial research (3,4) prompt speculation about correlations between Cu and biota that evolved there.

Metabolic Cu occurs as oxidized Cu(II) or reduced Cu(I). Its physiologic redox state controls Cu as a co-factor contributing to polypeptides that provide catalytic and electron transfer function in almost every known group of organisms alive today, from bacteria to mammals. Presently, over two dozen essential Cu proteins, some with porphyrin-Cu functional groups similar to porphyrin-iron association in hemoglobin, have been identified, each with its specific developmental or physiological function (1). Apparent Cu requirements and the ability to avoid its toxicity suggest Cu may have been available, required and used at the origin of life and continue as essential in certain roles throughout many, if not all, life forms. Some bacteria precipitate excess as aqueous forms of Cu on their cell membranes or walls (3).

Human content of 1.4-2.1 mg Cu/kg body weight is derived mostly from legumes, nuts, seeds and beef. Normal detoxification is metallothionein sequestration or expulsion via cellular pumping; resulting effluent is excreted. Copper toxicity is associated with Wilson's Disease and non-genetic chronic pulmonary disorders and cirrhosis. Human Cu-related health problems in the region will be described.

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Combined high precision Cu, Zn and Fe isotopes in mice brains

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Copper, Zn and Fe are essential elements in mammalian metabolism. For example, Cu and Fe work together in the formation of hemoglobin and red blood cells and Zn and Cu are involved in many enzymes in a number of functions. Moreover, several diseases can be linked to inbalances in these elements, e.g. Cu to Parkinson and prion diseases [1] and Zn to Alzheimers disease.

The analytical techniques needed to measure Cu and Zn isotopes precisely have only been developed in the last five years [2, 3, 4]. It has been highlighted that transition metal isotopes could be used to examine processes by which metals are transported through human bodies [5]. This implies that these isotopes could provide important insights into the pathways and controls on metals in biological substances. Such knowledge could be used to establish links between these metals and diseases.

Copper, Zn and Fe isotopes have been determined to high precision in mice brains from two different strains. The isotopes were measured by MC-ICPMS (Finnigan Neptune) at Bristol. The external reproducibility for Cu is ±0.09‰, for Zn ±0.08‰ and for Fe ±0.1‰.

δ^{56}Fe values vary between –1.44 and –2.67 relative to IRMM-014 and overlap with previously published Fe isotope variations in human blood [4]. δ^{65}Cu values range from –0.23 to –0.59 relative to NIST SRM 976 and δ^{66}Zn shows a variation from –0.25 to –0.42 relative to Lyon-JMC [2]. The fractionation and variation in Fe isotopes compared to Cu and Zn isotopes is large. Iron transport from blood into the brain is controlled by proteins [6]. This suggests a kinetic fractionation of the Fe isotopes. Copper, Zn and Fe isotope ratios in the mice brains from both strains, which had the same diet, overlap, and we therefore suggest that different mice strains have similar Cu, Zn and Fe isotopic compositions.

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