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Copper and iron uptake in continental hydrothermal systems

EVA ANDRADE-BARAHONA AND ALYSIA COX
Montana Technological University
Presenting Author: eandradebarahona@mtech.edu

Microorganisms inhabiting hydrothermal systems acquire metals such as copper (Cu) and iron (Fe) from their surroundings to perform many cellular processes and have been using these essential metal cofactors since early Earth. As Earth's atmosphere became oxygenated, Cu bioavailability increased and Fe bioavailability decreased [1, 2]. We measured Cu and Fe uptake in anoxic-suboxic sources and oxic outflows in Yellowstone National Park hydrothermal springs using low abundance enriched isotopes as tracers, or metal stable isotope probing (MSIP). We spiked water samples from six paired spring sources and outflow channels with ^{65}Cu and ^{57}Fe, incubated for four hours, then filtered onto 0.2-micron filters. After acid digestion, we calculated metal uptake rates from inductively coupled plasma - mass spectrometry measurements of ^{65}Cu and ^{57}Fe [3]. Uptake rates increased with pH, ranging from 2.38±0.09 to 413±9 $nmolL^{-1}d^{-1}$ for Cu in the outflows and from 2.90±0.13 to 1490±60 $nmolL^{-1}d^{-1}$ for Fe in sources and outflows, as a result of adsorption onto particulates. The alkaline "Bison Pool" in Sentinel Meadow exhibited a Cu uptake rate 13 times higher at the source than the outflow, likely caused by higher copper bioavailability. A combination of photosynthetic activity in the outflow channel and exposure to the atmosphere along the outflow yielded a dissolved oxygen concentration of $5.83x10^{-2}$ M, six orders of magnitude higher than in the suboxic spring source. Adsorption onto the particulate fraction at a source with pH 5.38±0.05 caused the highest Cu and Fe uptake rates, 4470±90 and 1490±60 $nmolL^{-1}d^{-1}$, respectively. Metal stable isotope probing experiments currently being analyzed included a field EDTA wash of the filters to distinguish between microbial uptake and adsorption onto the particulate fraction. Overall, all springs exhibited higher Cu uptake rates than Fe. These findings highlight that aqueous chemistry influences Cu and Fe uptake rates in hydrothermal systems and begin to provide insights into the evolution of metal uptake by hyperthermophiles facing increased oxidative stress in extreme environments.

[1] Ochiai EI (1983), *Biosystems 16*(2), 81-86. [2] Dupont *et al.* (2006), *PNAS 103*(47), 17822-17827. [3] Cox *et al.* (2014) *Mar. Chem. 166*,70-81.