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Metal Sequestration by Extracellular Peptides

MACON J. ABERNATHY[1], ALEXANDER JOHS[2], JEREMY SEMRAU[3], ALAN DISPIRITO[4], GRAHAM GEORGE[5], ERIC M PIERCE[2] AND RITIMUKTA SARANGI[1]

[1]SLAC National Accelerator Laboratory
[2]Oak Ridge National Laboratory
[3]University of Michigan
[4]Iowa State University
[5]University of Saskatchewan

Presenting Author: mjabern@slac.stanford.edu

Copper is key to the carbon cycle. Aerobic methane oxidizers utilize Cu in the oxidative catalysis of methane to methanol. In order to meet their Cu requirements, they have evolved a class of small, post-translationally modified peptides that are highly adept at Cu(II) acquisition and reduction. These peptides, termed methanobactins (mbs) are uniquely able to effect copper reduction, even in the presence of oxygen and facilitate the transport of bound Cu towards its final destination in methane monooxygenases. One such mb produced by Methylocystis sp. SB2 has shown promise in its ability to bind and sequester toxic metals, including Hg, but many aspects of its structural role in Cu acquisition are still unexplored. Here, we leveraged spectroscopic and computational approaches to investigate the multi-component mixture which results from the incubation of mb-SB2 with Cu(II), providing direct evidence for multiple Cu-SB2 binding modes, as well as evidence for a Cu(II)-SB2 species and multiple Cu(I)-SB2 species which are stabilized against re-oxidation. We demonstrate an electronic role for two primary functional groups in Cu binding, each of which contribute to the binding and stabilization of Cu(II) and Cu(I), and propose a mechanism for the formation of a 1 Cu(I):mb-SB2 dimer. The coexistence of these structures in solution provide a basis for cooperativity in Cu binding by SB2, and suggest the displacement of bound Cu(I) by Cu(II). We then extend this system to the binding of Zn, Cd and Hg by mb-SB2 to gauge the influence of the impact of this chalkophore on off-target, hazardous metals.