Goldschmidt2020 Abstract

# Spectroscopic Investigations of Late Transition Metal Complexation by Methanobactin Chalkophores

PETER ECKERT[1], ALEXANDER JOHS[1], AA DISPIRITO[3], JEREMY SEMRAU[2], BAOHUA GU[1], AND ERIC M. PIERCE[1]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA
2Civil & Environmental Engineering, The University of Michigan, Ann Arbor, MI 48109, USA
[3]Department of Biochemistry, Biophysics, and Molecular Biology, Iowa State University, Ames, IA 50011, USA

Methanotrophic bacteria catalyze the aerobic oxidation of methane to methanol using enzymes with copper (Cu)-based active sites, thereby exerting a modulating influence on the global methane cycle. To facilitate the acquisition of Cu ions some methanotrophic bacteria secrete small peptides known as methanobactins which strongly bind copper and function as an extracellular Cu recruitment relay analogous to siderophores and iron. In addition to Cu, methanobactins are known to form complexes with other late transition metals, including zinc (Zn) and mercury (Hg). Methanobactins are ideal candidates for spectroscopic study, but a detailed characterization of their spectroscopic features has not yet been undertaken, and the solution-phase interactions of methanobactins and late transition metals remains ambiguous. We present the first computational investigation of methanobactin peptides and compare it with experimental data from methanobactin-metal (i.e., Zn, Cu, and Hg) complexes. We describe the spectroscopic characteristics of the methanobactin-metal complexes and compare our experimental data with simulations of the coordination geometry. Drawing inspiration from previous investigations of the active site of the wild-type Green Fluorescent Protein, we propose a mechanism for a fluorescence enhancement observe upon mixing methanobactins with transition metals. Collectively, our results represent the first combined computational and experimental study of the spectroscopy of methanobactins and shed new light on coordination geometry and binding interactions that characterize methanobactin- metal (i.e., Zn, Cu, and Hg) complexes.