Oxygen Generation via Water Splitting by a Novel Biogenic Metal Binding Compound

Alan A. DiSpirito[1] (aland@iastate.edu), Philip Dershwitz[1], Nathan L. Bandow[1], Marcus T. McEllistrem[2], Rafael A. Heinze[2], Matheus Fonseca[2], Joshua C. Ledesma[1], Jacob R. Jennett[1], Ana M. DiSpirito[1], Navjot S. Athwal[1], Mark S. Hargrove[1], Thomas A. Bobik[1], Hans Zischka[3] and **Jeremy D. Semrau[4]**

[1]Roy J. Carver Department of Biochemistry, Biophysics and Molecular Biology. Iowa State University, Ames, IA; [2]Department of Chemistry, University of Wisconsin-Eau Claire, WI; [3]Institute of Molecular Toxicology and Pharmacology, Helmholtz Center Munich, German Research Center and Environmental Health, Ingolsteadter Landstrasse, Germany; [4]Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI

https://emmb.engin.umich.edu

Project Goals: The overall goal of this project is to determine how significant microbial competition for copper is *in situ*, particularly how such competition affects net methane and nitrous oxide emissions. By better understanding how microbes compete for trace nutrients (i.e., copper) at a molecular level, we can scale such competition to ecosystem functioning, i.e., how microbial competition can be modeled to predict emerging microbial community composition and activity. Doing so will enable us to better understand how interactions within microbial communities control net greenhouse gas emissions, and allow us to determine to what extent copper uptake systems may be public vs. private goods.

Abstract

Methanobactins (MBs) are small (<1,300 Da) post-translationally modified copper-binding peptides and represent the extracellular component of a copper acquisition system in some methanotrophs. Interestingly, MBs can bind a range of metals, with some reduced after binding, e.g., Cu^{2+} reduced to Cu^{+} and Au^{3+} to Au^{0}. Other metals, however, are bound but not reduced, e.g., K^{+}. The source of electrons for selective metal reduction has been speculated to be water but never empirically shown. Here, using $H_2{}^{18}O$, we show that when MB from *Methylocystis sp*. strain SB2 (MB-SB2) and *Methylosinus trichosporium* OB3b (MB-OB3) were incubated in the presence of either Au^{3+}, Cu^{2} , and Ag^{+}, $^{18,18}O_2$ and free protons were released. No $^{18,18}O_2$ production was observed either in presence of MB-SB2 or MB-OB3b alone, gold alone, copper alone, silver alone or when K^{+} or Mo^{2+} was incubated with MB-SB2. The discovery that MB will couple the oxidation of H_2O to metal reduction and the release of O_2 suggests that methanotrophs expressing MB may be able to maintain their activity in hypoxic/anoxic conditions through "self-generation" of dioxygen required for the initial oxidation of methane to methanol. Such an ability may be an important factor in enabling methanotrophs to not only colonize the oxic-anoxic interface where methane concentrations are highest, but also tolerate significant temporal fluctuations of this interface. Given that genomic surveys often show evidence of aerobic methanotrophs within anoxic zones, the ability to express MB (and thereby generate dioxygen) may be an important parameter in facilitating their ability to remove methane, a potent greenhouse gas, before it enters the atmosphere.

This work was supported by the Department of Energy, Award # DE-SC0020174.