

MANGANESE BIOSIGNATURES: MN(III) MINERAL FORMATION DURING MN(IV) OXIDE REDUCTION. N. Szeinbaum¹, S. Zhao², Y. Tang², C. Henny³, S.A. Crowe³, F.J. Stewart¹, T.J. DiChristina¹ and J.B. Glass², ¹School of Biological Sciences, Georgia Institute of Technology, Atlanta, GA (nadia@gatech.edu) ²School of Earth and Atmospheric Sciences, Georgia Institute of Technology, ³Department of Earth, Ocean, & Atmospheric Sciences, University of British Columbia, ⁴Research Center for Limnology, Indonesian Institute of Sciences, Cibinong, Indonesia

Background: Manganese (Mn) oxides are important paleo-redox proxies on Earth and extraterrestrial planets such as Mars (1, 2). Manganese has also recently been proposed as a biosignature for Mn²⁺-oxidizing microbial activity due to distinguishing mineralogical properties of biogenic and abiotic oxides (3). Microbial reduction of Mn(IV) oxides could also have the potential to generate biosignatures of microbial activity if long-lived biogenic Mn(III) phases are produced within minerals during the reduction process and can be distinguished from minerals produced through abiotic mechanisms. While the current paradigm of the Mn cycle assumes that Mn(IV) oxides are completely reduced to Mn²⁺ during anaerobic microbial respiration, Mn(III) is formed as an intermediate during Mn(IV) reduction (4), and a recent study found that the Mn(III) could remain as a long-lived mineral phase under carbon limitation (5). Thus, the type and availability of organic carbon may influence production of potential biosignatures during Mn(IV) reduction.

Methods: We established an enrichment culture using sediments from Lake Matano, a metal-rich, ancient ocean analog that may harbor microbes able to oxidize methane coupled to Mn(IV) reduction (6, 7). Organic carbon in Lake Matano is mostly mineralized via methanogenesis before reaching the iron-rich sediments, limiting organic matter bioavailability for metal-reducers (8). Enrichment cultures were established with methane as the only electron donor and Mn(IV) as the only acceptor, and transferred periodically under anoxic conditions. Mn²⁺ was measured voltammetrically and solid manganese was characterized by XRD analysis. Methane oxidized was quantified by measuring the evolution of ¹³C-dissolved inorganic carbon (DIC). Community composition was determined via 16S rRNA amplicon analysis using MOTHUR.

Findings: Cultures incubated with methane and Mn(IV) were enriched in facultative (*Comamonadaceae* and *Rhodocyclaceae*) and strict (*Geobacter*) anaerobes. XRD spectra of a red-brown precipitate from year-long Mn(IV)-reducing enrichment cultures showed Mn(III)-like XRD peaks (Fig 1).

Implications: Mn(III) is formed as an intermediate during Mn(IV) reduction, and may become a long-lived phase within the mineral. Biogenic Mn(III) phases may indicate presence of metal-reducing microbial activity, present or past, on future missions to Mars and exoplanets. Manganese mineral biosignatures could also be informative in explaining widespread and abundant solid Mn(III) in the Earth's geologic rock record before the Great Oxidation Event (9).

Future directions: Further studies will be aimed at uncovering whether the Mn(III) mineral phase is formed from a one-electron reduction from Mn(IV), or abiotic Mn²⁺ interactions with Mn(IV). We will also investigate the source of electrons for metal reduction.

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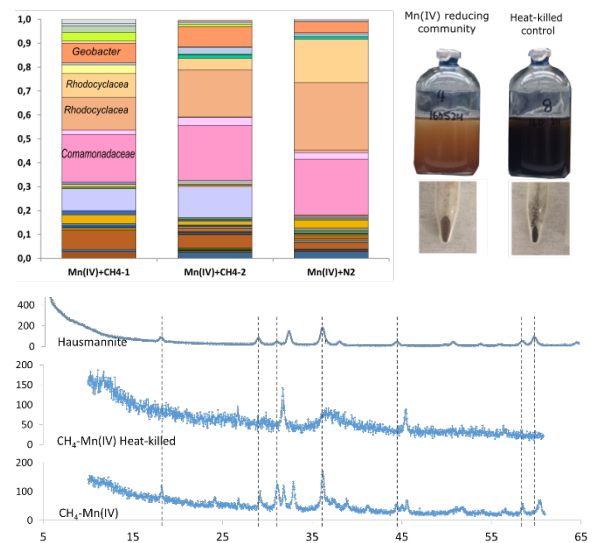


Figure 1. (Top) Visual inspection in *Comamonadaceae*-*Rhodocyclaceae*- and *Geobacter*-enriched (but not heat-killed) incubations suggest that Mn(IV)-reducing communities produce red Mn(III)-bearing minerals, compared to black birnessite. (Bottom) Preliminary XRD results indicate that hausmannite (Mn(II,III)) was produced during Mn(IV) reduction. Peak alignments between the hausmannite standard and the enrichment culture are indicated by dashed lines.

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