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Mn-oxidizing microorganisms oxidize environmental Mn(II) producing Mn(IV)-oxides. *Pseudomonas putida* MnB1 is a widely studied organism for the oxidation of manganese (II) to manganese (IV) by a multicopper oxidase. The biogenic manganese oxides (BMOs) produced by MnB1 and similar organisms have unique properties compared to non-biological manganese oxides. Along with an amorphous, poorly crystalline structure, previous studies have indicated that BMOs have high surface areas and high reactivities. It also known that abiotic Mn-oxides promote oxidation of organics and have been studied for their water oxidation catalytic function. For this proposed work, MnB1 is grown and maintained, and subsequently transferred to culturing media containing manganese (II) salts to observe the oxidation of manganese (II) to manganese (IV). We have shown that we can achieve water oxidation via whole-cell catalysis by a recently published peer-reviewed article in *Life* journal. Our experiments have led us to explore evolutionary implications of the origin of water oxidizing organisms.

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μ₄-oxo bridges between the Mn centers²³. Alternatively, Taguchi et al. (2014) theorized that the OEC could be approximated by a Mn complex in the presence of Ca²⁺ ions²⁴. The Ca-OH bond on

Results from this ongoing project has been published in *Life* journal,²⁵ but to put succinctly, we know the size, morphology, composition, and catalytic water oxidation of the whole-cell BMOs and these were compared to abiotic manganese oxides showing better water oxidizing capabilities.

Investigations into the water oxidizing capabilities will take place by two methods. Specific Aim #1: Culturing MnB1 under various metal concentrations in an effort to improve water oxidation capabilities by incorporation of redox-benign metals. Specific Aim #2: Expression and purification of the multicopper oxidase from the MnB1 gene, *cumA*

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- (17) Hocking, R. K.; Brimblecombe, R.; Chang, L.-Y.; Singh, A.; Cheah, M. H.; Glover, C.; Casey, W. H.; Spiccia, L. Water-Oxidation Catalysis by Manganese in a Geochemical-like Cycle. *Nat. Chem.* **2011**, *3* (6), 461–466. <https://doi.org/10.1038/nchem.1049>.
- (18) Kwon, K. D.; Refson, K.; Sposito, G. On the Role of Mn(IV) Vacancies in the Photoreductive Dissolution of Hexagonal Birnessite. *Geochim. Cosmochim. Acta* **2009**, *73* (14), 4142–4150. <https://doi.org/10.1016/j.gca.2009.04.031>.
- (19) Soldatova, A. V.; Balakrishnan, G.; Oyerinde, O. F.; Tebo, B. M.; Spiro, T. G. Biogenic and Synthetic MnO₂ Nanoparticles: Size and Growth Probed with Absorption and Raman Spectroscopies and Dynamic Light Scattering. *Environ. Sci. Technol.* **2019**, *53* (8), 4185–4197. <https://doi.org/10.1021/acs.est.8b05806>.
- (20) Brouwers, G.-J.; Cornelis, P.; Baysse, C. CumA, a Gene Encoding a Multicopper Oxidase, Is Involved in Mn²⁺ Oxidation in *Pseudomonas putida* GB-. *APPL ENV. MICROBIOL* **1999**, *65*, 7.
- (21) Geszvain, K.; McCarthy, J. K.; Tebo, B. M. Elimination of Manganese(II,III) Oxidation in *Pseudomonas putida* GB-1 by a Double Knockout of Two Putative Multicopper Oxidase Genes. *Appl. Environ. Microbiol.* **2013**, *79* (1), 357–366. <https://doi.org/10.1128/AEM.01850-12>.
- (22) Iyer, A.; Del-Pilar, J.; King'ondou, C. K.; Kissel, E.; Garces, H. F.; Huang, H.; El-Sawy, A. M.; Dutta, P. K.; Suib, S. L. Water Oxidation Catalysis Using Amorphous Manganese Oxides, Octahedral Molecular Sieves (OMS-2), and Octahedral Layered (OL-1) Manganese Oxide Structures. *J. Phys. Chem. C* **2012**, *116* (10), 6474–6483. <https://doi.org/10.1021/jp2120737>.
- (23) Menezes, P. W.; Indra, A.; Littlewood, P.; Schwarze, M.; Göbel, C.; Schomäcker, R.; Driess, M. Nanostructured Manganese Oxides as Highly Active Water Oxidation Catalysts: A Boost from Manganese Precursor Chemistry. *ChemSusChem* **2014**, *7* (8), 2202–2211.