

# Timothy E. Machonkin

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## EDUCATION

- 1989-1993 Honors B.S. Chem. and B.S. in Cellular & Molecular Biology, *University of Michigan*  
Undergraduate Honors Thesis: "Reactivity of Mononuclear Dichloro-Manganese(IV) Schiff Base Complexes Towards Alkenes"  
Advisor: Vincent L. Pecoraro
- 1993-2000 Ph.D. in Inorganic Chemistry, *Stanford University*  
Ph.D. Dissertation: "Spectroscopic and Biochemical Studies of Multicopper Oxidases Involved in Iron Metabolism"  
Advisor: Edward I. Solomon
- 2000-2003 NIH Postdoctoral Fellow, *University of Wisconsin*  
Research Area: Paramagnetic NMR methodology and studies of human [2Fe-2S] ferredoxin  
Advisor: John L. Markley

## PROFESSIONAL EXPERIENCE

- 2003-2006 Assistant Professor, University of Rochester, Dept. of Biochemistry & Biophysics
- 2006-12 Assistant Professor, Whitman College, Dept. of Chemistry
- 2010-2011 Visiting Scientist, University of British Columbia, Dept. of Microbiology & Immunology
- 2012-present Associate Professor, Whitman College, Dept. of Chemistry
- Fall 2013 Visiting Scientist, University of Michigan, Depts. of Chemistry and Biological Chemistry

## TEACHING EXPERIENCE

- 1993-1997 Stanford University. Teaching assistant, Head teaching assistant, and Instructor for the Stanford Summer Science and Math Institute (an intensive three-week program for incoming underrepresented-minority students). Guest Lecturer for Coordination Chemistry.
- 2003-2006 University of Rochester. Lecturer for Biochemistry, Structural Biology, and Advanced Enzymology.
- 2006-present Whitman College. Course instructor for General Chemistry I & II, General Chemistry Lab I & II, Advanced General Chemistry, Quantitative Analysis, Inorganic Chemistry, Advanced Synthesis Laboratory, Bioinorganic Chemistry, and Chemistry Seminar.

## RECENT RESEARCH MENTORING EXPERIENCE

- 2003-2006 University of Rochester. Five undergraduates, three technicians, and one graduate student (jointly with a faculty member in Chemistry).

2006-present Whitman College. 30 undergraduates. Many students have gone to PhD programs in Chemistry or related fields (at Wisconsin, Yale, Chicago, U. Washington, etc.), some to medical school, and one to an MD/PhD program). Others work in various fields, including management consulting and in industry.

### **HONORS, FELLOWSHIPS, AND AWARDS**

1993 Honors in Chemistry  
 1993 American Institute of Chemists Award for Outstanding Senior Chemistry Major  
 1993 Phi Beta Kappa  
 1993-1996 National Science Foundation Predoctoral Fellowship  
 1996-1997 Stanford University Lieberman Fellowship  
 1997 Award for Outstanding Freshmen/Sophomore Academic Advisor  
 2000-2003 National Institutes of Health Postdoctoral Fellowship  
 2005-2006 NYSTAR Watson Investigator (one of 10 per year in New York)  
 2010 Visiting Scientist Award, University of British Columbia Life Sciences Institute  
 2012 G. Thomas Edwards Faculty Award for Excellence in Teaching and Scholarship

### **COLLEGE SERVICE**

2006-present Active member of Whitman's Phi Beta Kappa chapter, served one term each as vice-president and president  
 2007-2010 Member, Academic Information Technology Advisory Group (chair, 2009-2010)  
 2008 Member, Innovation in Teaching Grant Selection Committee  
 2008-2010 Academic Advisor & Faculty Mentor to two College Success Foundation Achievers students  
 2009-present System Administrator for the 400 MHz Bruker Avance III NMR spectrometer  
 2011-2014 Member, Library Committee (chair 2012-2013)  
 2011, 2015-2016 Member, Howard Hughes Medical Institute grant proposal exploratory committee  
 2012-2015, 2017-2018 Chair of the Chemistry Department  
 2013-2016 Member, Quantitative Reasoning & Literacy Working Group  
 2014-2017 Member, Curriculum Committee (served on three subcommittees)  
 2015 Member, Provost Search Committee  
 2016-2018 Faculty mentor in Whitman's formal new faculty mentoring program  
 2016-2018 2019-2022 Member, Whitman's Scholars at Risk Committee (chair, 2019-2022)  
 2017-2018, 2022-2023 Chair of the Board of Review  
 2017-2021 Member, Whitman's Beckman Scholars Program organizing committee (chair, Spring 2017)

**ADDITIONAL PROFESSIONAL ACTIVITIES**

Reviewer for various journals, including *J. Am. Chem. Soc.*, *J. Biol. Inorg. Chem.*, *J. Inorg. Biochem.*, *FEBS Lett.*, *Biochemistry*, *PLOS One*, *Science Reports* and *Inorg. Chem.*

Reviewer for grant applications for NSF and other funding agencies

Session chair at ACS National Meetings for the Inorganic Division (multiple years)

External evaluator for several applications for tenure and promotion

**PUBLICATIONS** (underlined coauthors indicate Whitman undergraduate students)

Law, N.A., Machonkin, T.E., McGorman, J.P., Larson, E.J., Kampf, J.W., and Pecoraro V.L. (1995) A Structurally Characterized Dichloro-Manganese(IV) Complex Capable of Halogenating Alkenes, *J. Chem. Soc. Chem. Commun.*, 2015-2016.

Solomon, E.I., Sundaram, U.M., and Machonkin, T.E. (1996) Multicopper Oxidases and Oxygenases, *Chem. Rev.* 96, 2563-2605.

Solomon, E.I., Machonkin, T.E., and Sundaram, U.M. (1997) Spectroscopy of Multi-Copper Oxidases, in *Multi-Copper Oxidases*, (Messerschmidt, A., ed.), pp 103-128, World Scientific, Singapore.

Root, D.E., Henson, M.J., Machonkin, T.E., Mukherjee, P., Stack, T.D.P., and Solomon, E.I. (1998) Electronic and Geometric Structure of a Trinuclear Mixed-Valence Copper (II, II, III) Cluster, *J. Am. Chem. Soc.* 120, 4982-4990.

Machonkin, T.E., Zhang, H.-H., Hedman, B., Hodgson, K.O., and Solomon, E.I. (1998) Spectroscopic and Magnetic Studies of Human Ceruloplasmin: Identification of a Redox-Inactive Reduced Type 1 Copper Site, *Biochemistry* 37, 9570-9578.

Solomon, E.I., Palmer, A.E., Sundaram, U.M., and Machonkin, T.E. (1998) Spectroscopic Studies of O<sub>2</sub> Intermediates in Copper Proteins: Electronic Structure Contributions to Function in Bioinorganic Chemistry, in *Spectroscopic Methods in Bioinorganic Chemistry*, (Solomon, E.I. and Hodgson, K.O., eds), pp 423-452, ACS Symposium Series, Vol. 692.

Machonkin, T.E., Musci, G., Zhang, H.-H., Bonaccorsi di Patti, M.C., Calabrese, L., Hedman, B., Hodgson, K.O., and Solomon, E.I. (1999) Investigation of the Anomalous Spectroscopic Features of the Copper Sites in Chicken Ceruloplasmin: Comparison to Human Ceruloplasmin, *Biochemistry* 38, 11093-11102.

Machonkin, T.E. and Solomon, E.I. (2000) The Thermodynamics, Kinetics, and Molecular Mechanism of Intramolecular Electron Transfer in Human Ceruloplasmin, *J. Am. Chem. Soc.* 122, 12547-12560.

Machonkin, T.E., Quintanar, L., Palmer, A.E., Hassett R., Severance S., Kosman D.J., and Solomon E.I. (2001) Spectroscopy and Reactivity of the Type 1 Copper Site in Fet3p from *Saccharomyces cerevisiae*: Correlation of Structure With Reactivity in the Multicopper Oxidases, *J. Am. Chem. Soc.* 123, 5507-5517.

Machonkin, T.E., Westler, W.M., and Markley, J.L. (2002) <sup>13</sup>C{<sup>13</sup>C} 2D NMR: A Novel Strategy for the Study of Paramagnetic Proteins with Slow Electronic Relaxation Rates, *J. Am. Chem. Soc.* 124, 3204-3205.

Machonkin, T.E. and Markley, J.L. (2002) Electron-Nuclear Interactions, in *Encyclopedia of Nuclear Magnetic Resonance*, Vol. 9, (Grant, D.M. and Harris, R.K., eds.), pp 384-401, Wiley, Chichester.

Machonkin, T.E., Mukherjee, P., Henson, M.J., Stack, T.D.P., and Solomon, E.I. (2002) The EPR Spectrum of a Cu(II/II/III) Cluster: Anisotropic Exchange in a Bent Cu(II)<sub>2</sub>O<sub>2</sub> Core, *Inorg. Chim. Acta* 341, 39-44.

Lin, I.-J., Gebel, E.B., Machonkin, T.E., Westler, W.M., and Markley, J.L. (2003) Correlation Between Hydrogen Bond Lengths and Reduction Potentials in *Clostridium pasteurianum* Rubredoxin, *J. Am. Chem. Soc.* 125, 1464-1465.

Machonkin, T.E., Westler, W.M., and Markley, J.L. (2004) Strategy for the Study of Paramagnetic Proteins with Slow Electronic Relaxation Rates: Application to Oxidized Human [2Fe-2S] Ferredoxin, *J. Am. Chem. Soc.* 126, 5413-5426.

Park I.Y., Eidsness M.K., Lin I.-J., Gebel E.B., Youn B., Harley J.L., Machonkin T.E., Frederick R.O., Markley J.L., Smith E.T., Ichiye T., and Kang C.H. (2004) Crystallographic Studies of V44 Mutants of *Clostridium pasteurianum* Rubredoxin: Effects of Side-chain Size on Reduction Potential”, *Proteins Struct. Funct. Bioinf.* 57, 618-625.

Machonkin, T.E., Westler, W.M., and Markley, J.L. (2005) Paramagnetic NMR Spectroscopy and Density Functional Calculations in Analysis of the Geometric and Electronic Structures of Iron-Sulfur Proteins, *Inorg. Chem.* 44, 779-797.

Lin, I.-J., Gebel, E.B., Machonkin, T.E., Westler, W.M., and Markley, J.L. (2005) Changes in Hydrogen-bond Strengths Explain Changes in the Reduction Potentials of a Series of 10 Rubredoxin Variants, *Proc. Natl. Acad. Sci. U.S.A.* 102, 14581-14586.

Rocks, S.S., Brennessel, W.W., Machonkin, T.E., and Holland, P.L. (2009) Solid-state and Proton NMR Characterization of an Iron(II) Complex of a Tridentate, Facially Coordinating N,N,O Donor Ligand, *Inorg. Chim. Acta* 362, 1387-1390.

Lin, I.-J., King, D.S., Machonkin, T.E., Westler, W.M., and Markley, J.L. (2009) Hyperfine-shifted  $^{13}\text{C}$  and  $^{15}\text{N}$  Resonances from *Clostridium pasteurianum* Rubredoxin: Assignments and Interpretation, *J. Am. Chem. Soc.* 131, 15555-15563.

Machonkin, T.E., Holland, P.L., Smith, K.N., Liberman, J.S., Dinescu, A., Cundari, T.R., and Rocks, S.S. (2010) Determination of the Active Site of *Sphingobium chlorophenicum* 2,6-Dichlorohydroquinone dioxygenase (PcpA), *J. Biol. Inorg. Chem.* 10, 291-301.

Rocks, S.S., Brennessel, W.W., Machonkin, T.E., and Holland, P.L. (2010) Solution and Structural Characterization of Iron(II) Complexes with *Ortho*-Substituted Phenolates: Insights Into Potential Substrate Binding Modes in Hydroquinone Dioxygenases, *Inorg. Chem.* 49, 10914-10929.

Machonkin, T.E. and Doerner, A.E. (2011) Substrate Specificity of *Sphingobium chlorophenicum* 2,6-Dichlorohydroquinone 1,2-Dioxygenase, *Biochemistry* 50, 8899-8913.

Machonkin, T.E., Boshart M.D., Schofield, J.A., Rodriguez, M.M., Grubel, K., Rokhsana, D, Brennessel, W.W., Holland, P.L (2014) Structural and Spectroscopic Characterization of Iron(II), Cobalt(II), and Nickel(II) *Ortho*-Dihalophenolate Complexes: Insights into Metal-Halogen Secondary Bonding, *Inorg. Chem.* 53, 9837-9848.

Schofield, J.A., Brennessel, W.W., Urnezus, E., Rokhsana, D., Boshart M.D., Juers, D.H., Holland, P.L., Machonkin, T.E. (2015) Metal-halogen Secondary Bonding in a 2,5-Dichlorohydroquinonate Cobalt(II) Complex: Insights Into Substrate Coordination in the Chlorohydroquinone Dioxygenase PcpA, *Eur. J. Inorg. Chem.*, 4643-4647.

Burrows, J.E., Paulson, M.Q., Altman E.R., Vukovic, I. Machonkin, T.E. (2019) The Role of Halogen Substituents and Substrate  $\text{p}K_a$  in Defining the Substrate Specificity of 2,6-Dichlorohydroquinone 1,2-Dioxygenase (PcpA), *J. Biol. Inorg. Chem.* 24, 575-589

Kipouros, I., Stańczak, A., Culka, M., Andris, E., Machonkin, T.E, Rulisek, L., Solomon, E.I. (2022) Evidence for H-bonding Interactions to the  $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxide}$  of Oxy-tyrosinase that Activate its Coupled Binuclear Copper Site, *Chem. Commun.*, 3913-3916.

**RECENT TALKS AND POSTER PRESENTATIONS**

“PcpA: Defining a Preference for Halogen Substituents in a Ring-Cleaving Dioxygenase” American Chemical Society National Meeting, San Diego, CA, 2012 (invited talk).

“Pesticide-Eating Bacteria and an Enzyme That is Specific for Halogenated Aromatic Molecules” Western Washington University, WA 2012 (invited talk).

“Metal-Halogen Secondary Bonding in Iron(II), Cobalt(II), and Nickel(II) 2,6-Dihalophenolate Complexes: Insights into the Substrate Specificity of the Hydroquinone Dioxygenase PcpA” American Chemical Society National Meeting, New Orleans, LA, 2013 (talk).

“Exploring the Substrate Specificity of the 2,6-Dichlorohydroquinone Ring-cleaving Dioxygenase PcpA Through Biochemical and Model Chemistry Approaches” International Conference on Bioinorganic Chemistry, Grenoble, France, 2013 (poster).

“Defining a Preference for Halogen Substituents in the Ring-Cleaving Dioxygenase PcpA” University of Michigan, Ann Arbor, MI, 2013 (invited talk).

“Metal-halogen Secondary Bonding in Iron(II), Cobalt(II), and Nickel(II) 2,6-Dihalophenolate Complexes: Insights into the Substrate Specificity of the Hydroquinone Dioxygenase PcpA” American Chemical Society National Meeting, Dallas, TX, 2014 (talk).

“Exploring the Substrate Specificity of the 2,6-Dichlorohydroquinone Ring-Cleaving Dioxygenase PcpA Through Biochemical and Model Chemistry Approaches” Washington State University, Pullman, WA, 2015 (invited talk).

“Defining a Preference for Polarizable Halogen Substituents in the Hydroquinone Ring-Cleaving Dioxygenase PcpA” PacifiChem, Honolulu, HI, 2015 (talk).

“Defining a Preference for Polarizable Halogen Substituents in the Hydroquinone Ring-Cleaving Dioxygenase PcpA” Montana State University, Bozeman, MO, 2016 (invited talk)

“Research at a Liberal Arts College: A Ring-Cleaving Dioxygenase Enzyme with a Preference for Polarizable Halogen Substituents” University of Chicago, Chicago, IL, 2016 (invited talk)

“Hydroquinone Ring-Cleaving Dioxygenase: Enzymes and Model Complexes” American Chemical Society National Meeting, Washington, DC, 2017 (invited talk)

“Hydroquinone Ring-Cleaving Dioxygenase: Enzymes and Model Complexes” ACS Northwest Regional Meeting (NORM), Richland, WA, 2018 (invited talk)

“A Tale of Two Hydroquinone Ring-Cleaving Dioxygenases: PcpA from *Sphingobium chlorophenolicum*, and PnpC1C2 from *Pseudomonas putida* DLL-E4” Metals in Biology Gordon Conference, Ventura, CA, 2019 (poster).

“A Tale of Two Hydroquinone Ring-Cleaving Dioxygenases: PcpA from *Sphingobium chlorophenolicum*, and PnpC1C2 from *Pseudomonas putida* DLL-E4” International Conference of Biological Inorganic Chemistry 19, Interlaken, Switzerland, 2019 (invited talk and poster).

“PcpA: A Dihalohydroquinone Ring-Cleaving Dioxygenase”, Max Planck Institute für Kohlenforschung, Mülheim, Germany, 2019 (invited talk).

“A Tale of Two Hydroquinone Ring-Cleaving Dioxygenases: Enzymes Involved in Pollutant Degradation”, Whitman College Faculty Forum, Walla Walla, WA, 2020 (talk)

“Exploration of Ring-Cleaving Dioxygenases: Enzymes Involved in Pollutant Degradation”, Whitman College Summer Science Café, Walla Walla, WA, 2022 (invited talk)

“A Mutagenesis Study of the Active Site of PnpC1C2, A Hydroquinone Ring-Cleaving Dioxygenase”, International Conference of Biological Inorganic Chemistry 20, Adelaide, Australia, 2023 (poster).

**RECENT EXTRAMURAL GRANTS**

- 2006-2009 American Chemical Society—Petroleum Research Fund “G” Grant  
“Understanding the Origin of Suicide Inactivation in the Extradiol Dioxygenases”  
P.I., \$35,000 over 2 years, with a 1-year no-cost extension
- 2006-2009 M.J. Murdock Charitable Trust Start-up Grant  
P.I., \$25,000 over 2 years, with a 1-year no-cost extension
- 2007-2010 National Science Foundation—Major Research Instrumentation Grant  
“MRI: Acquisition of an X-ray Diffraction Instrument for Interdisciplinary and  
Collaborative Research and Education in an Undergraduate Setting”  
Co-P.I., \$464,934 over 3 years
- 2009-2012 National Science Foundation—Major Research Instrumentation Grant  
“MRI: Acquisition of a 400 MHz NMR Spectrometer for Undergraduate Research and  
Research Training”  
Co-P.I., \$389,000 over 3 years
- 2010-2014 National Science Foundation—Research At Undergraduate Institutions Grant  
“RUI: The Sources of Substrate Specificity in Hydroquinone Dioxygenases”  
P.I., \$259,000 over 3 years (plus one year no-cost extension)
- 2010-2011 University of British Columbia Life Sciences Institute Visiting Scholar Award  
\$10,000
- 2015-2020 National Science Foundation—Research At Undergraduate Institutions Grant  
“RUI: The Sources of Substrate Specificity in Hydroquinone Dioxygenases”  
P.I., \$385,000 over 3 years (plus two one-year no-cost extensions)
- 2019-2022 Beckman Scholars Program  
(This is an institutional grant that supports four undergrad research students.)  
\$104,000 over 3 years
- 2021-2024 M.J. Murdock Charitable Trust Bridge Grant  
“The Hydroquinone Ring-Cleaving Dioxygenase PnpC1C2: Mechanistic  
Characterization and Reengineering for Activity Towards Novel Substrates”  
P.I., \$70,000 over 3 years
- 2022-2023 M.J. Murdock Charitable Scientific Research Grant  
“Acquisition of Two Instruments for Multi-Disciplinary Research and Teaching”  
co-P.I., \$115,287
- 2022-2025 National Science Foundation—Research At Undergraduate Institutions Grant  
“RUI: Re-engineering Ring-Cleaving Dioxygenases for Activity Towards Novel  
Substrates”  
P.I., \$240,000 over 3 years