

Spectroscopic Characterization and Comparison of the Binuclear Non-Heme Ferrous sites in m-Ferritin and S-Nitric Oxide Reductase

Jennifer K. Schwartz¹, Xiaofeng Liu², Elizabeth C. Theil², Radu Silaghi-Dumitrescu³, Donald M. Kurtz, Jr.³, and Edward I. Solomon¹.

¹*Department of Chemistry, Stanford University*, ²*Center for BioIron at CHORI (Children's Hospital Oakland Research Institute)*, and ³*Department of Chemistry and Center for Metalloenzyme Studies, University of Georgia*.

Binuclear non-heme iron proteins catalyze a diverse range of reactions. These reactions involve the activation of dioxygen and most recently, nitric oxide, at a largely conserved diiron active site. Relatively little is known about the electronic and geometric structure of the ferrous sites in *Moorella thermoacetica* flavodiiron protein (FprA) and Bullfrog m-ferritin (mFr). Ferritin is a spherical 480 kDa protein made up of 24 monomers, which form a hollow center. The ferroxidase site present in each monomer catalyzes the oxidation of Fe(II) to a ferric-oxo mineral precursor which is then removed from the ferroxidase site and stored in the core of the protein as ferric oxide(1). The FprA has been shown to function as a scavenging nitric oxide reductase (S-NOR) in anaerobic bacteria, reducing two NO molecules to water and N₂O (2). A combination of circular dichroism (CD), magnetic circular dichroism (MCD), and variable-temperature, variable-field MCD (VTVH MCD) have been used to probe the Fe(II) binding to these active sites, as well as the zero-field splitting and the exchange-coupling between the irons due to their coordination environment and bridging ligation (3). These data provide greater understanding of the structure/function correlations between these enzymes and further elucidate their overall reactivity and reaction pathways.

1. Liu, X.; Theil, E. C.; *Acc. Chem. Res.*; **2005**, 38(3), 167-175.
2. Silaghi-Dumitrescu, R.; Coulter, E. D.; Das, A.; Ljungdahl, L. G.; Jameson, G. N. L.; Huynh, B. H.; Kurtz, D. M., Jr.; *Biochem.*; **2003**, 42(10), 2806-2815.
3. Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S.-K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y.-S.; Zhou, J.; *Chem. Rev.*; **2000**, 100(1), 235-350.

This research is supported by NSF-MCB-9214214.