X-ray Absorption Spectroscopy of Mn Enzymes

Eileen Y. Yu, Pamela J. Riggs-Gelasco, Timothy L. Stemmler, Charles F. Yocum, and James E. Penner-Hahn
The University of Michigan, Ann Arbor, Michigan, USA

Manganese redox enzymes are crucial in a variety of biological systems including the photosynthetic oxidation of H_2O to O_2, the disproportionation of hydrogen peroxide, and the disproportionation of superoxide. The Mn sites in these systems have been characterized using x-ray absorption spectroscopy. The photosynthetic oxygen evolving complex (OEC) shows approximately two 2.7-Å Mn-Mn interactions characteristic of di-μ-oxo bridged Mn dimers. These binuclear-like sites can be selectively reduced by the appropriate choice of reductant, leading to formation of two spectroscopically distinct reduced species. A similar di-μ-oxo bridged binuclear site is found in superoxidized Mn catalase, although with nearest neighbor ligation that is clearly distinct from that in the OEC. The OEC and reduced Mn catalase contain EXAFS detectable Mn-Mn interactions at 3.3-3.4 Å; similar features are not found in other binuclear Mn enzymes. The similarities and differences between these binuclear sites will be discussed. Recently, we have found that treatment of the OEC with fluoride and turnover of Mn catalase in the presence of fluoride both lead to the reversible formation of species in which the Mn site has been reduced, as judged by the XANES energy. Possible interpretations of these observations will be discussed.