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Radiation Damage and Mn Metalloproteins

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Manganese complexes play critical roles in the metabolism of oxygen that is important in many biological systems. Among these systems, one of the most important is the photo-induced oxidation of water to dioxygen by the photosynthetic membrane protein complex, Photosystem II (PS II). This reaction is catalyzed by a Mn_4CaO_5 cluster located in the PS II membrane complex. One other system is a catalase that contains a binuclear Mn cluster, that disproportionates peroxide to water and dioxygen.

We have shown previously by X-ray spectroscopy that the Mn_4Ca cluster is highly susceptible to the X-ray radiation damage, particularly under the condition that the diffraction data have been commonly collected [1]. We have detailed XAS studies as a function of dose, temperature, energy, and time. We have also completed a similar X-ray damage study using XAS of the oxidized and reduced Mn catalase.

Recently, the crystal structure of PS II isolated from thermophile was reported at a resolution of 1.9 A [2] by collecting the data at much lower X-ray dose than that has been used for the earlier PSII crystallography studies. The electron density map clearly shows the geometry of the four metals and one Ca. Their study for the first time gives us a starting point to think about the detailed chemical structure of the Mn_4CaO_5 cluster in the dark state (S_1) and also the consequence of specific radiation damage to the redox-active Mn site. The crystal structures of the Mn catalase have also been reported with high resolutions (~ 1 A) [3,4].

We have compared the effect of X-ray radiation damage on the two major Mn metalloprotains, PS II and Mn catalase. We discuss possible differences between these two cases. The study also gives us an insight into the unique effect of radiation damage to individual metalloproteins and the importance of the combination of the spectroscopic techniques and crystallography in order to obtain intact forms of the catalytic complexes [1,5].

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Radiation Damage to Protein Crystals is Reduced with a Micron-sized X-ray Beam

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The small, intense X-ray beams available at 3rd generation light sources have been exploited by structural biologists to determine the structure of increasing larger or more complex macromolecules. The crystals of many of these macromolecules may have a largest dimension of only 5-10 microns, and may diffract poorly due to lack of internal order. Obtaining data of high signal-to-noise requires exposing the crystal to a beam of high flux density, resulting in increased absorbed dose and radiation damage. Although cryo-cooling of protein crystals significantly reduces X-ray induced radiation damage, it does not eliminate the damage.

The predominant mechanism of interaction of an X-ray with a low-Z atom in the crystal is the emission of a photoelectron, which carries away most of the energy of the incident X-ray. When the emitted photoelectron scatters off another atom, it loses energy to the atom resulting in local damage. As the photoelectron energy decreases, the probability of interacting with yet another atom increases causing more frequent interactions until finally the photoelectron is recaptured. Thus, if the X-ray beam size is small compared to the distance the photoelectron travels from its point of emission, then deposition of photoelectron energy outside the beam footprint may reduce radiation damage inside the beam footprint. Monte-Carlo simulations predict that a photoelectron of typical energy could travel 4 – 5 μm from the point of emission before being absorbed. We studied radiation damage to lysozyme crystals by monitoring the diffracted intensity of 18.5-keV X-rays as a function of dose and beam size (0.86 – 15.6 μm) at beamline 23-ID-B at the Advanced Photon Source. We observed a 3-fold reduction of damage per dose within the footprint of the smallest compared to the largest beam. In addition, the spatial extent of radiation damage was mapped using both 15.1- and 18.5-keV X-rays and a ~1-μm beam. The damage profiles displayed spatial anisotropy with greater damage occurring along the direction of the X-ray polarization, as expected. The spatial extent of the damage was limited to about 4 μm.

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The Role of Hydrogen in Radiation Damage

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Radiation damage of biological samples is a major impediment to the success of experiments using ionizing radiation. In a recent study