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Time and dose resolved crystallography to control and capture redox states in heme peroxidases

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Metalloenzymes containing heme centres catalyse a wide range of reactions critical to life. Understanding the structure and electronic states of the heme centre across multiple functionally relevant states is essential to understand mechanism. I will describe work using time resolved serial crystallography as well as the use of X-ray dose for the manipulation of heme iron oxidation states in dye decolourising peroxidases [1] using multiple, complementary, serial crystallography and single-crystal spectroscopic approaches.

Fixed target drop-on-chip, tape drive droplet on demand and correlated spectroscopies allow the formation of high valent Fe(IV) states to be characterised. X-ray Pump Probe serial femtosecond crystallography (SFX) together with dose-resolved serial synchrotron crystallography (SSX) allowed the peroxidases to be driven between multiple iron oxidation states that can be spectroscopically validated. Intriguingly, the formation and dose response of the Fe(IV)-O state is highly variable between the chemically identical heme groups of the homo-oligomeric proteins highlighting the importance of understanding the effect of the crystalline lattice on observed changes in time- and dose-resolved crystallography experiments.

Lucic, M. et al (2021) Aspartate or arginine? Validated redox state X-ray structures elucidate mechanistic subtleties of FeIV = O formation in bacterial dye-decolorizing peroxidases. JBIC 27 (7), 743-761.

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