Lytic polysaccharide monooxygenases; a history and insights into current progress

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Biological conversion of plant biomass depends on peroxygenases and peroxidases acting on insoluble polysaccharides and lignin. Among these are cellulose- and hemicellulose-degrading lytic polysaccharide monooxygenases (LPMOs), which have revolutionized our concept of biomass degradation. In the CAZy database, LPMOs are categorised into eight of the seventeen auxiliary activity (AA) families (AA9-11 and AA13-AA17) based on sequence similarities. Despite large differences between the sequences of LPMOs in these different families, there are several conserved features evident in the secondary structure that unify all LPMOs. Central to LPMOs is an active site comprising a universally conserved histidine brace where a copper-ion is coordinated by three nitrogen ligands. Today, the prevailing view on the reaction catalyzed by LPMOs entails that the LPMO-Cu(II) is first reduced to LPMO-Cu(I) by a priming reduction step, followed by binding of H_2O_2 and homolytic cleavage. This is believed to generate a Cu-bound hydroxide species and a hydroxyl radical where the latter abstracts a hydrogen from the Cu-bound hydroxide to generate a Cu(II)-oxyl species, the formation of which is generally accepted. The Cu(II)-oxyl species then abstracts a hydrogen from the C-H bond of either C1 or C4 of the carbohydrate substrate, followed by hydroxylation of the bond, ultimately destabilizing the bond and leading to glycosidic bond cleavage. The lecture will briefly go through the history prior to the LPMO discovery, the transition of LPMOs to be viewed as monooxygenases to be peroxygenases, and key enzymatic features allowing the powerful catalysis of hydroxylation of saturated C-H bonds.

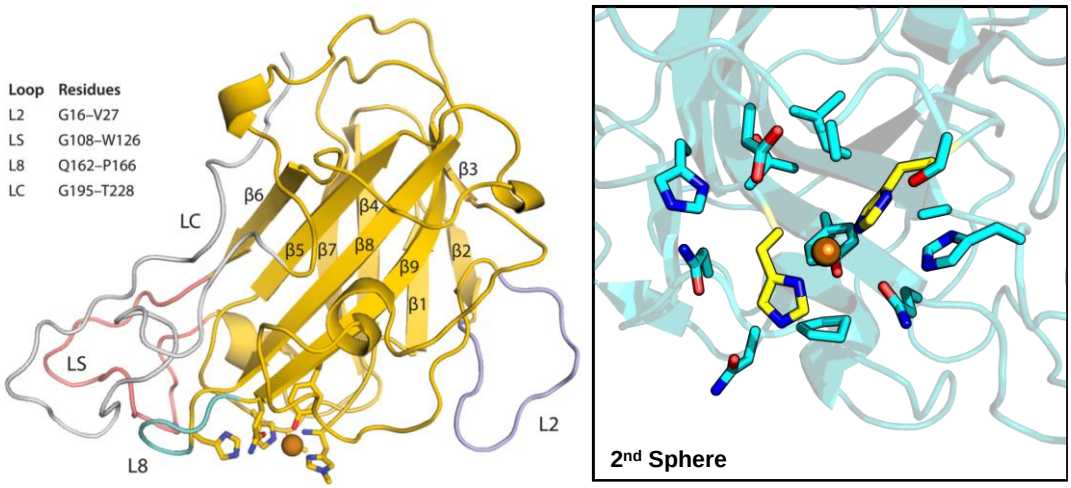

Figure 1. Crystal structure of an LPMO and possible 2nd sphere residues.