Hydrogenases and barriers for biotechnological hydrogen production technologies

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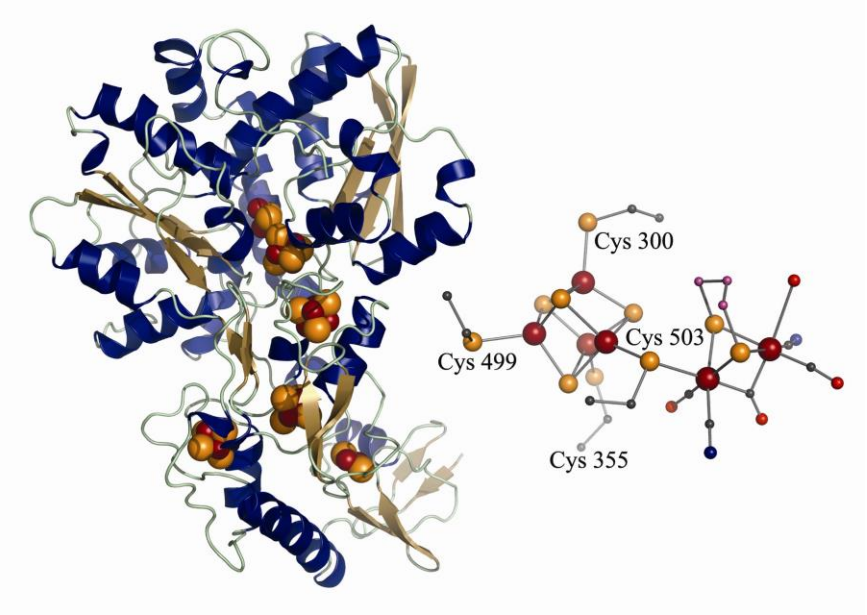
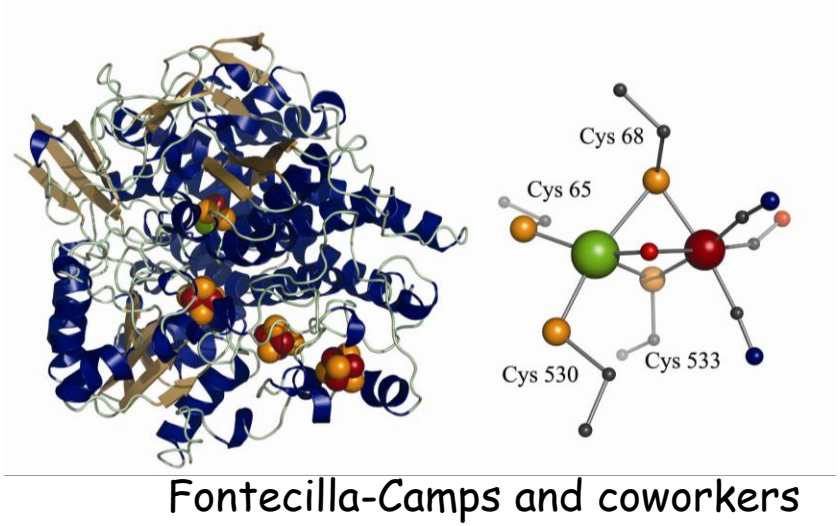
Hydrogenases ($2e^- + H^+ <-> H_2$)– the most profound case of convergence evolution?

[FeFe]-hydrogenases
- **Bacteria**
- **Lower Eukaryotes**

[NiFe]-hydrogenases
- Bacteria
- Archaea
- Cyanobacteria





Fontecilla-Camps and coworkers

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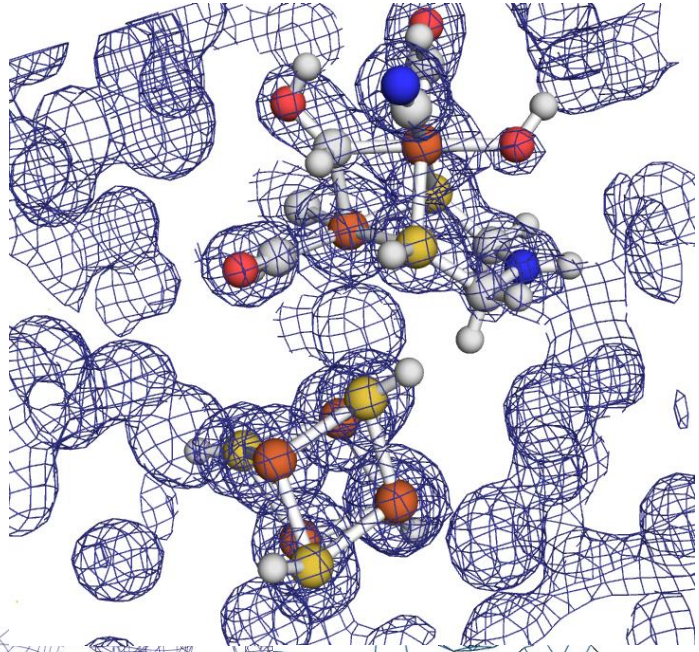
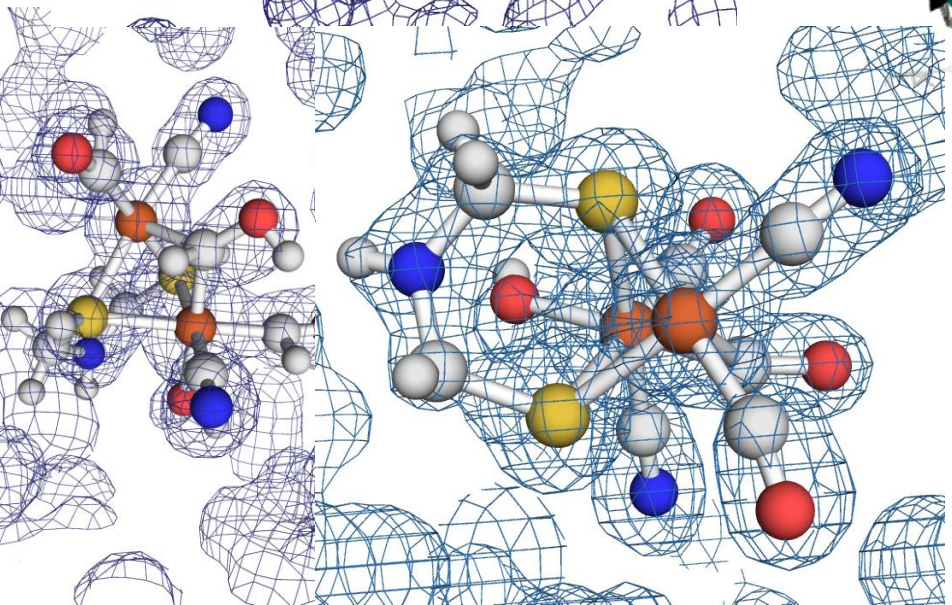
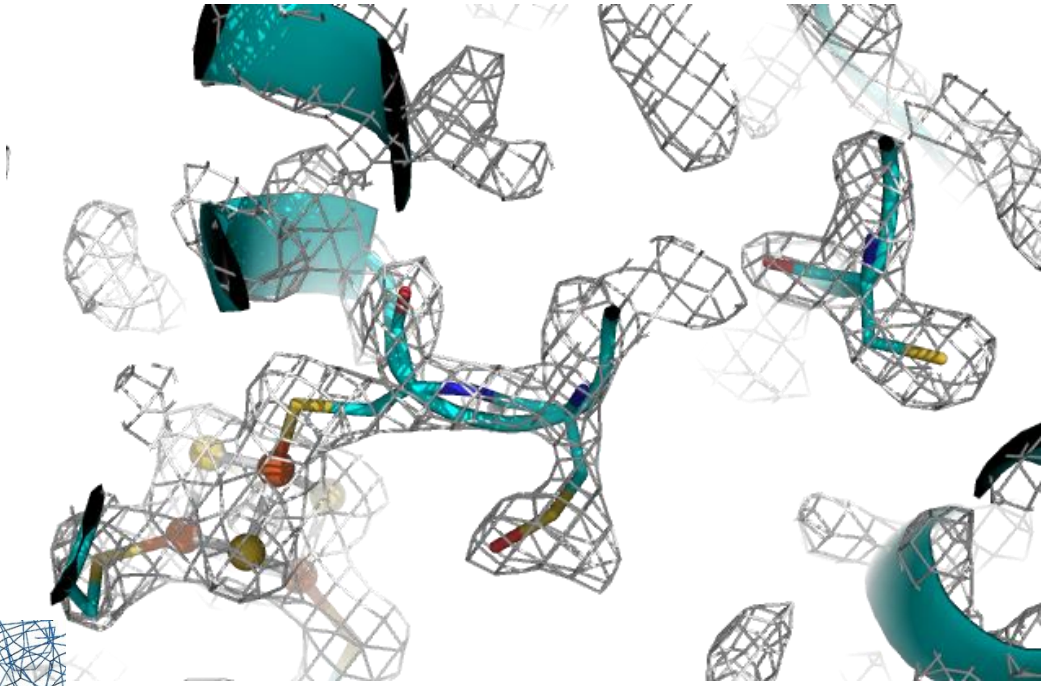
Active site metal clusters sensitive to oxygen

Oxygen inactivation
- degradation of active site cluster

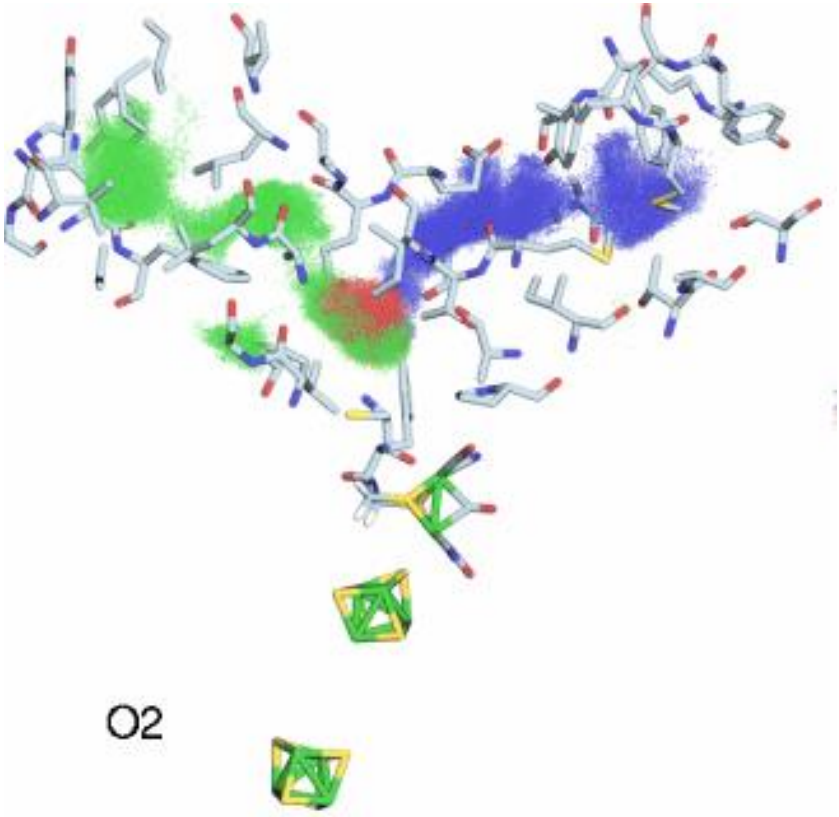




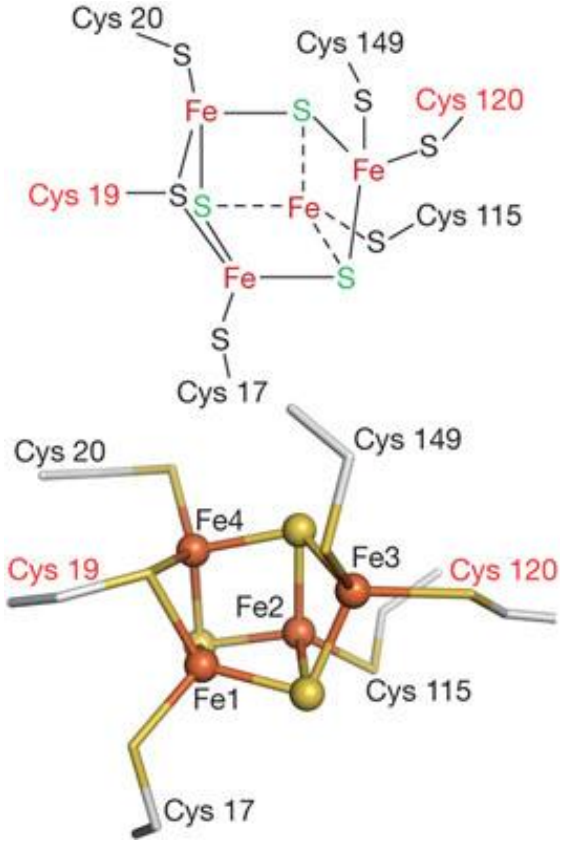


[FeFe]-hydrogenase H cluster degraded by loss of 2Fe subcluster followed by loss of [4Fe-4S] cluster – activity can be restored in metal free enzyme through reconstitution followed by in vitro activation

Oxygen sensitivity
– access of oxygen to active site

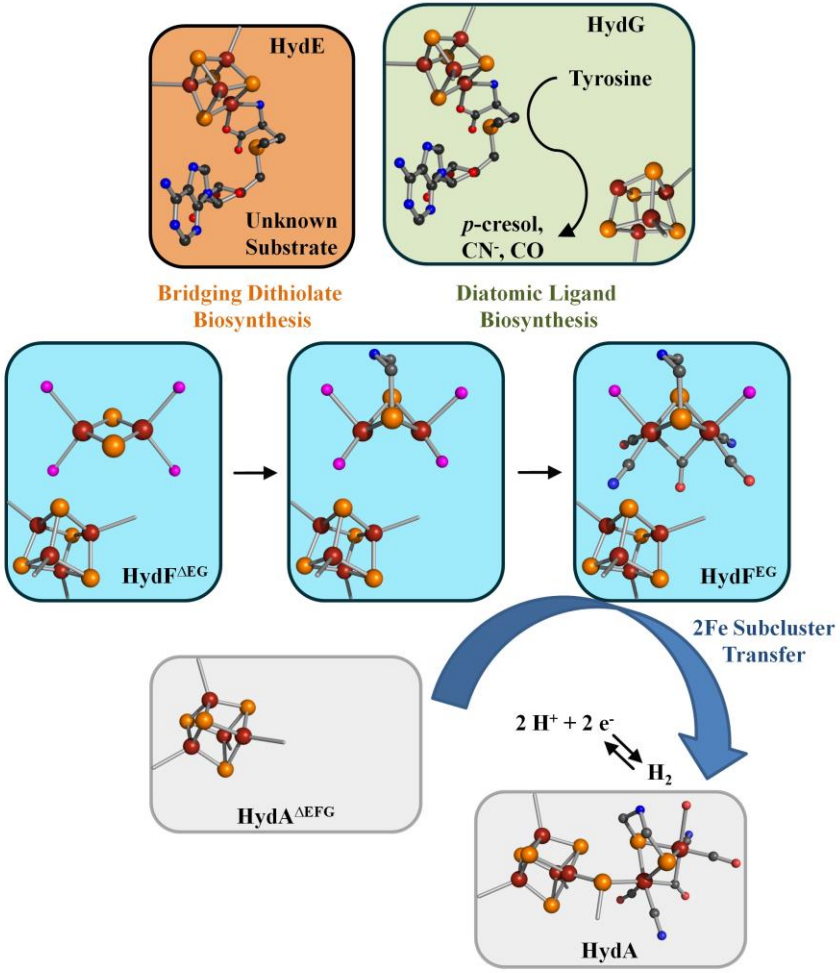


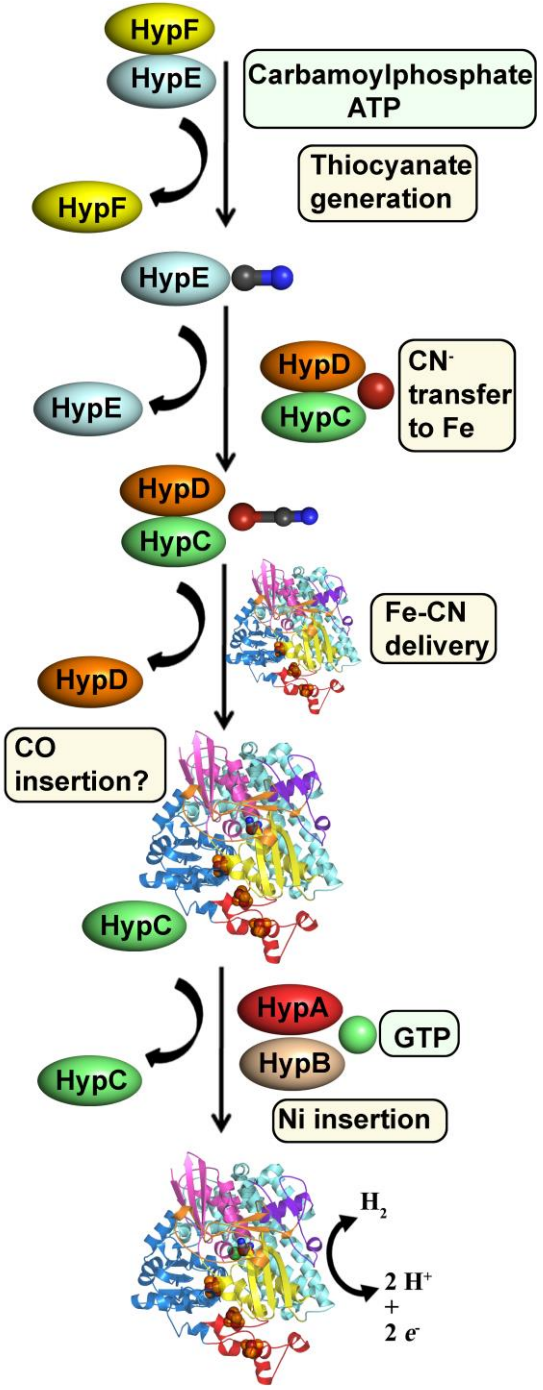
O_2 access in the [FeFe]-hydrogenase from *Clostridium pasteurianum* – Schulten and coworkers



Unique FeS cluster involved in O_2 tolerance in [NiFe]-hydrogenases

Active site biosynthesis and cluster maturation





Critical information for engineering / heterologous expression

Defining integration into metabolism (electron transfer pathways) and the best model organisms