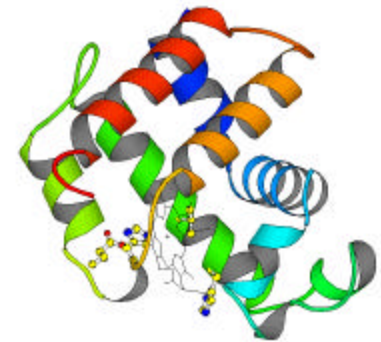


Dehaloperoxidase: Old structure, New function

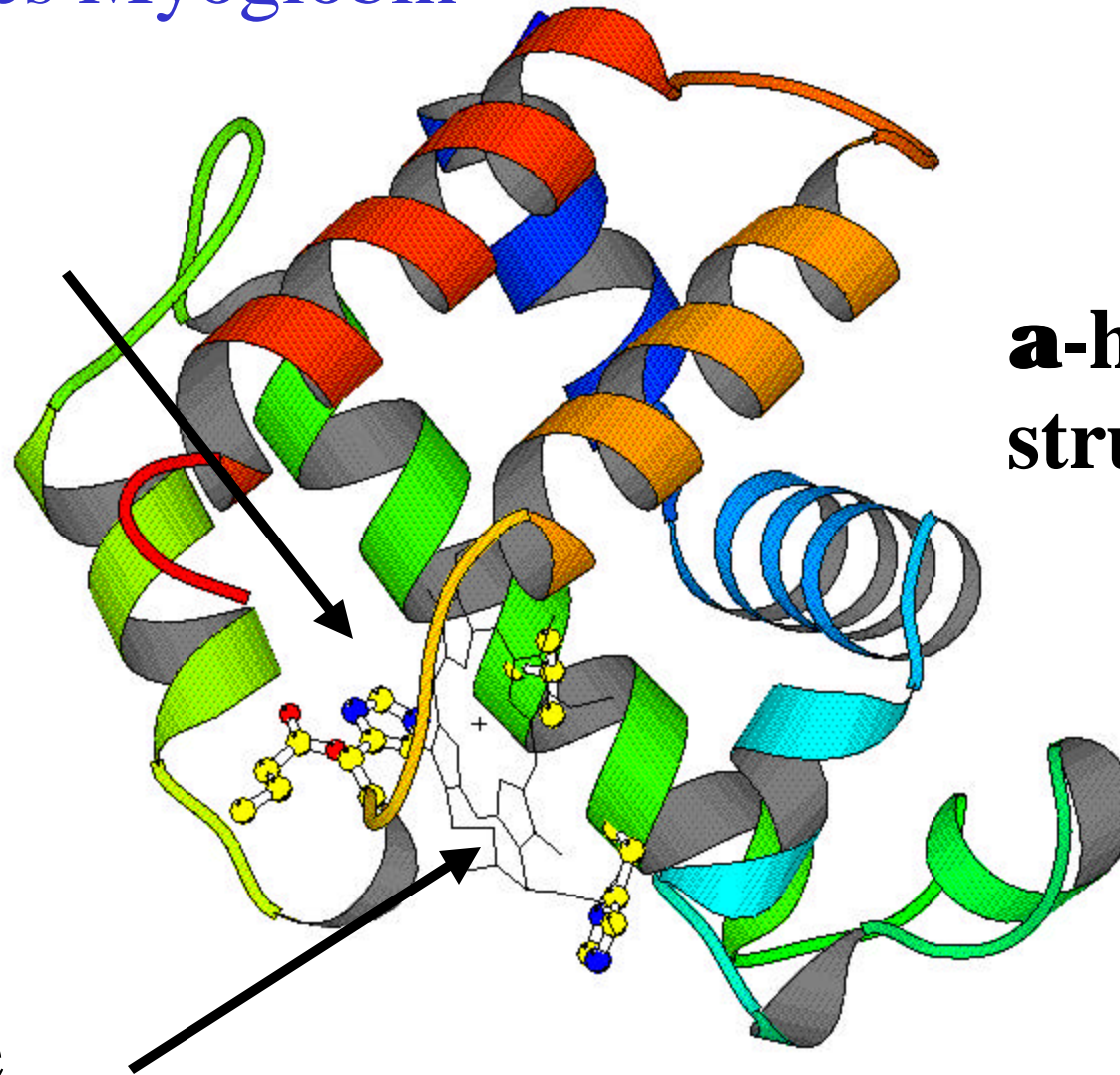
Dehaloperoxidase is a new enzyme found in marine worm *Amphitrite ornata*

The structure strongly resembles myoglobin
Sequence homology with globins is low



Dehaloperoxidase Structure Resembles Myoglobin

Proximal
Histidine

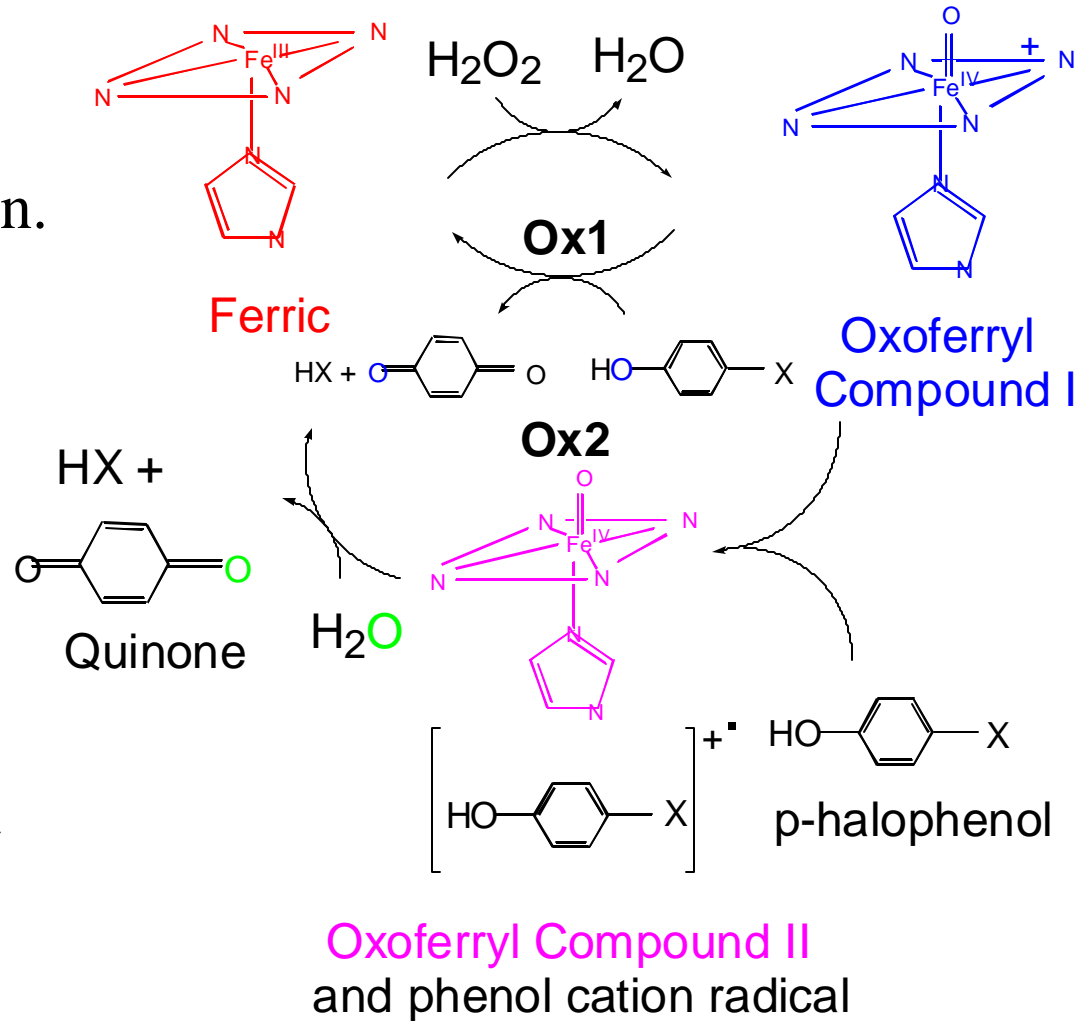


**α -helical
structure**

Heme

Dehaloperoxidase looks like Mb, but dehalogenates halophenols

The mechanism is still under investigation.
 The Ox1 pathway is a peroxidase reaction.
 The Ox2 pathway is a monooxygenase pathway.
 The structural similarity with myoglobin is interesting in light of the function of this enzyme.



Resonance Raman studies of the axial ligand vibration show a correlation between oxygen activation and frequency

Deoxy hemoglobin 212 cm^{-1} Low O_2 affinity

Myoglobin 219 cm^{-1} Intermediate affinity

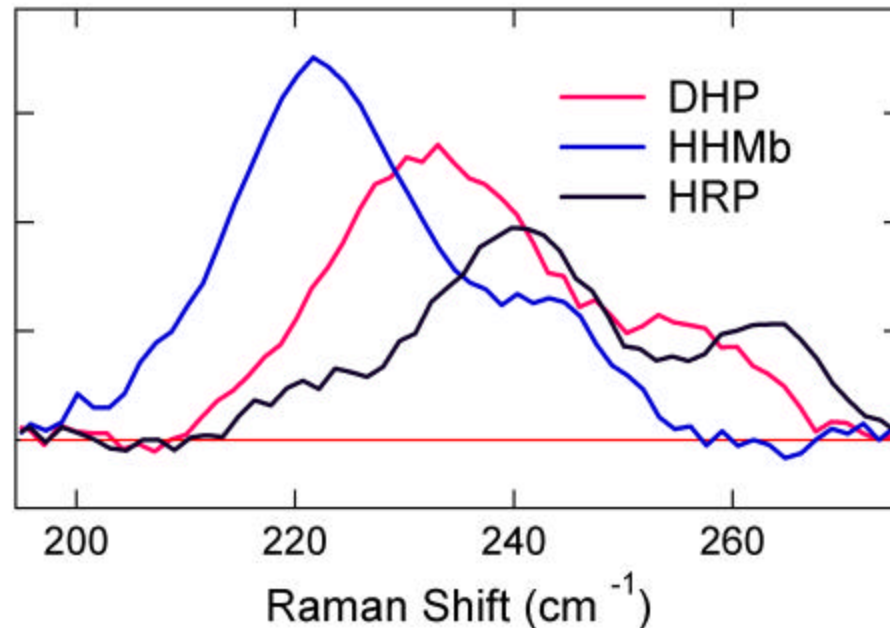
R-state hemoglobin 223 cm^{-1} High O_2 affinity

Support heterolytic O-O cleavage

Horseradish peroxidase 245 cm^{-1} Activates peroxide

Supports homolytic O-O cleavage

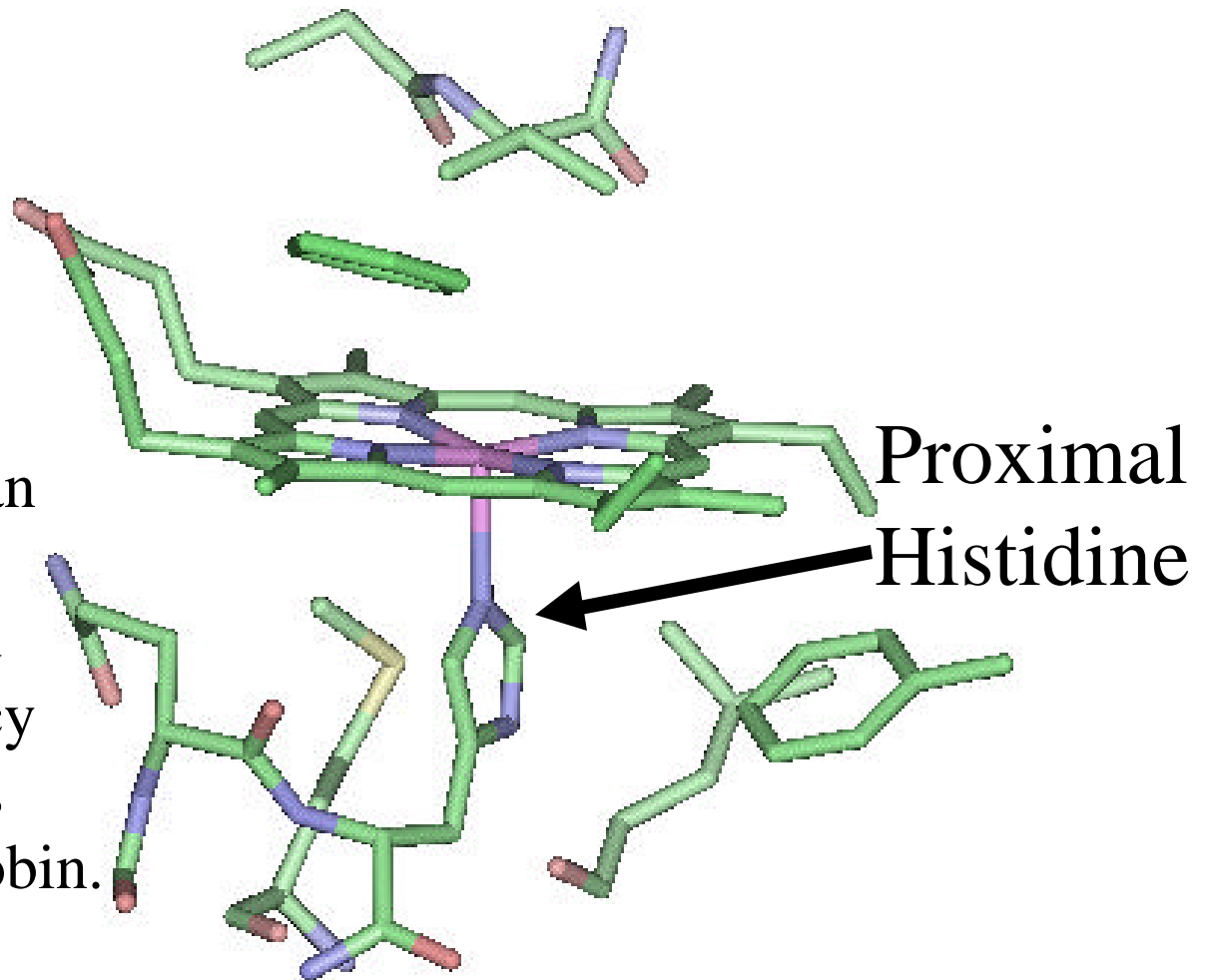
Resonance Raman spectroscopy of iron-histidine stretching mode of deoxy dehaloperoxidase



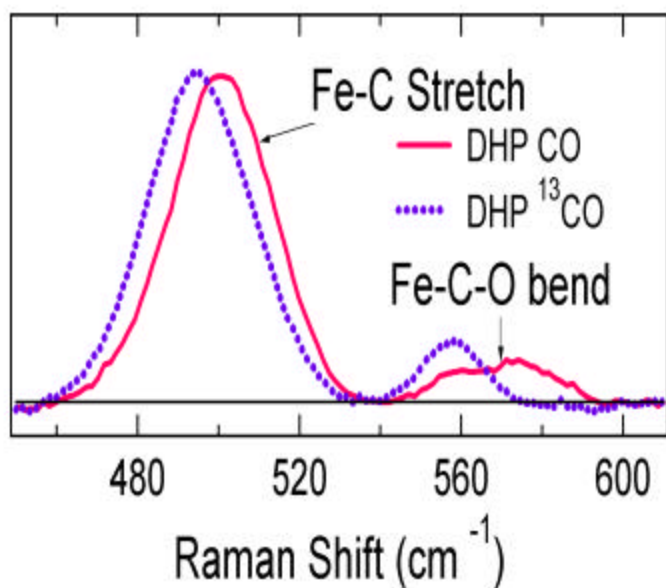
The frequency of the Fe-His mode is intermediate between that of myoglobin (HHMb) and horse radish peroxidase (HRP).

The X-ray structure shows a hydrophobic pocket for the proximal histidine

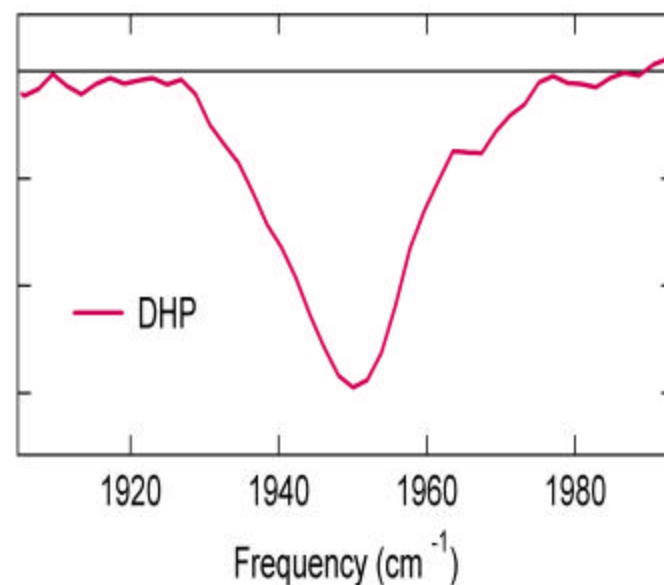
Although there are differences in certain residues, the hydrogen bonding of the proximal histidine to the C=O group of leucine 83 is stronger than H-bonding found in globins. The observed iron-histidine frequency of $233 \pm 2 \text{ cm}^{-1}$. This is higher than for any globin.



Vibrational Spectroscopy of the CO form of dehaloperoxidase



Resonance Raman spectra showing Iron-CO stretching and bending modes.



FTIR spectrum showing the C-O stretching vibration in dehaloperoxidase.

The data follow the π -backbonding correlation for globins rather than peroxidases

Based on the ^{13}CO shifts the Fe-CO stretching vibration is assigned at $499\pm 2\text{ cm}^{-1}$.

The C-O stretch is observed at $1950\pm 2\text{ cm}^{-1}$.

These values are consistent with the observed π -backbonding correlation in globins, but not peroxidases.

Although DHP has structural and spectroscopic similarities to myoglobin its sequence homology is low.

A pairwise alignment of the sequence for sperm whale myoglobin (1MBC) and dehaloperoxidase (1EW6) from the Protein Data Bank shows an identity of only 17.3 %!

Research continues to understand the unusual reactivity of this enzyme.

The structural and spectroscopic similarities with myoglobin provide a unique opportunity to test many of the hypotheses relevant to the role of structure/function relationships that have been derived from biophysical studies.