Redox Chemistry of Tungsten and Iron-Sulfur Prostetic Groups in *Pyrococcus furiosus* Formaldehyde Ferredoxin Oxidoreductase.

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Detailed redox chemical studies through spectroscopic monitoring have previously been carried out for *P. furiosus* aldehyde oxidoreductase and glyceraldehyde-3-phosphate oxidoreductase, but not for formaldehyde oxidoreductase (FOR). However, FOR of the close relative *Thermococcus litoralis* has been scrutinized. When the gene sequences of the FOR's from *P. furiosus* and *T. litoralis* are compared a very high similarity and identity is found.

The two subsequent reduction potentials of tungsten, $E_1'^0$(VI/V) and $E_2'^0$(V/IV) are usually quite close in value, and, in fact, frequently crossed over (i.e. $E_1 < E_2$) compliant with the 'non metal' nature of the elements. Therefore dye mediated redox titrations and additional non-equilibrium substrate titrations were performed to exhibit the tungsten species.

The present study on *P. furiosus* FOR does not only explore to what (surprisingly limited) extent protein homology translates into homologous redox chemistry, but it also addresses a number of unsolved questions related to active site multiplicity and the thermodynamic and kinetic (in)stability of the W(V) form.