From low- to high-potential bioenergetic chains: Thermodynamic constraints of Q-cycle function

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The electrochemical parameters of all cofactors in the supercomplex formed by the Rieske/cytb complex and the SoxM/A-type O$_2$-reductase from the menaquinone-containing Firmicute *Geobacillus stearothermophilus* were determined by spectroelectrochemistry and EPR redox titrations. All redox midpoint potentials ($E_m$) were found to be lower than those of ubi- or plastoquinone-containing systems by a value comparable to the redox potential difference between the respective quinones. In particular, $E_m$ values of +200 mV, -360 mV, -220 mV and -50 mV (at pH 7) were obtained for the Rieske cluster, heme $b_L$, heme $b_H$ and heme $c_i$, respectively. Comparable values of -330 mV, -200 mV and +120 mV for hemes $b_L$, $b_H$ and the Rieske cluster were determined for an anaerobic Firmicute, *Helio bacterium modesticaldum*. Thermodynamic constraints, optimization of proton motive force build-up and the necessity of ROS-avoidance imposed by the rise in atmospheric O$_2$ 2.5 billion years ago are discussed as putative evolutionary driving forces resulting in the observed redox upshift. The close conservation of the entire redox landscape between low and high potential systems suggests that operation of the Q-cycle requires the precise electrochemical tuning of enzyme cofactors to the quinone substrate as stipulated in P. Mitchell’s hypothesis.