that alone justifies the huge cost of maintaining a small quasi-autonomous genetic system in the chloroplast.

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C1/4 Energy and informational fluxes in evolution — The key to complexity in the biosphere

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Two great fluxes control the biosphere, — energy and information. Evolution, behavior, cellular recognition and signaling, and human communication are examples of the latter. Shannon recognized that information transmission required two components, engineering aspects and the semantic content or 'meaning' of the message. This semantic component cannot be quantified within the same thermodynamic framework as bioenergetic aspects. The message needs a thermodynamic carrier, but the meaning has value only in context and after translation and interpretation. These characteristics lead to some interesting conclusions about the role of semantic transmission in the development of complexity through evolution, and in human culture. Translation is essential, both mechanistically, and because it allows an increase in combinatorial potential through dimensionality. Exploitation of combinatorial potential is constrained by the evolutionary heritage, so that the biosphere shares a highly restricted informational base, which increases in complexity with time. In humans, complexity is extended to the cultural domain. Genetic and cultural channels for inheritance have different components, but they share a common feature in their need for a semantic component, and matching translational machineries, and this justifies a Universal Darwinism. This leads to a view of the evolutionary process in terms of success in exploitation of thermodynamic potential through an exploration of the nature of reality; — a molecular epistemology encapsulated in the commonality of life.

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(C2) Controversial issues in cytochrome oxidase colloquium lecture abstracts

C2/1 Controversial issues and conformational changes in cytochrome *c* oxidase

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Despite high resolution structures and powerful spectral and computational methods for analysis of terminal oxidases, the molecular mechanism remains contentious. Areas at issue include the pathways and key residues involved in proton movement, the timing of proton uptake and release with respect to electron transfer, the role of water clusters as proton acceptors, regulatory mechanisms and the nature of catalytic intermediates. Another subject of conflicting views and data is whether significant conformational changes are involved in the coupling mechanism. Small, localized changes, or no changes in structure upon complete reduction have been reported previously. We have solved the structures of resting, reduced and re-oxidized forms of *Rhodobacter sphaeroides* CcO at 2.0–2.2 Å. The reduced form shows little change in overall structure, but the entire porphyrin ring of heme a_3 and its hydroxyl-farnesyl tail are shifted 1–3 Å, opening the top of the K proton channel and impacting critical residues in the K path. Also in the K-channel region, a high occupancy binding site for the bile acid deoxycholate is resolved. Bile acids are strong inhibitors of the bovine C*c*O and a binding site is found in the same location as in *Rs*C*c*O. The results suggest that redox state-induced conformational change, and a conserved steroid binding site, could regulate proton uptake in the K path. (NIH GM26916; MSU REF03-016).

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C2/2 Rapid kinetic studies of electron transfer in cytochrome oxidase

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The 1-electron reduction of pulsed, oxidized cytochrome oxidase was investigated using a new photoactive binuclear ruthenium complex, $[Ru(bipyrazine)_2]_2$(quaterpyridine), (Ru_2Z). The photoexcited state Ru(II*) of Ru_2Z is reduced by aniline to Ru(I), which then reduces Cu_A with yields up to 60%. The pulsed O_H state of cytochrome oxidase was prepared by a stopped-flow-flash technique. Mixing fully reduced anaerobic enzyme with oxygenated buffer containing Ru_2Z resulted in formation of the oxidized O_H state within 5 ms. Ru_2Z was then excited with a laser flash to inject 1 electron into Cu_A. Electron transfer from Cu_A to heme a occurred with a rate constant of 20,000 s^{-1} in the bovine oxidase, followed by electron transfer from heme a to Cu_B with rate constants of 750 s^{-1} and 110 s^{-1} and 63% completion. The extent of electron transfer from heme a to Cu_B was only 30% in the non-pulsed O form, indicated a significant difference between the pulsed O_H and non-pulsed O form of bovine oxidase. In contrast, pulsing did not have a significant effect on electron transfer in *Rhodobacter sphaeroides* cytochrome oxidase. The role of electrostatics in controlling electron transfer in cytochrome oxidase has also been explored.

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C2/3 A redox coupled proton pumping mechanism for the B-type cytochrome *c* oxidases: Density functional studies of the *ba*$_3$-oxidase from *Thermus thermophilus*

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The aim of our work is to derive a mechanism of proton pumping by the heme-copper oxidases. After a brief introduction to structural details of *ba*$_3$-oxidase concerning the oxygen-uptake channel, the oxygen-in to water-out event, and the nature of the active-site, Fe_{a3}–Cu_B pair, evidence will be presented to support only one proton uptake path from the inside, namely a modified K-path. The bulk of the talk will focus on Density Functional Theory calculations of an ~200-atom active-site model, and thermochemical deductions therefrom, that support a novel, fourteen-step, chemically-detailed, redox-coupled mechanism for proton-pumping by the B-type oxidases. An explana-