Electron flow in bacterial multi-heme cytochromes

M. BREUER[1], D.M.A. SMITH[2], J. BLUMBERGER[1] AND K.M. ROSSO[2]*

[1]University College London, London, UK
[2]Pacific Northwest National Laboratory, Richland, WA, USA (*correspondence: kevin.rosso@pnnl.gov)

Understanding mechanisms and kinetics of electron transfer processes in environmental systems is an important frontier for molecular theory and computation. This presentation addresses elementary aspects of predicting electron transfer rates, demonstrates the essentiality of computational molecular simulation relative to lacking experimental probes, and establishes a new methodological state-of-the-art for this purpose, using bacterial multi-heme electron transfer proteins as the case study.

Electron transport to extracellular solid metal oxides by metal-reducing bacteria is a fundamental biogeochemical process optimized by evolution to catalytic perfection. To shed light into why and how individual electron transfer steps in associated multi-heme cytochromes are combined into overall molecular function, we carried out extensive computer simulations of the recently crystallized decaheme cytochrome MtrF. We report redox potentials of individual hemes, reorganization energies and electronic coupling matrix elements for heme-to-heme electron transfer in MtrF explicitly solvated in water. The free energy profile for electron flow along various evident heme 'wire' pathways was computed using thermodynamic integration and classical molecular dynamics, and could be related to differences in the charged amino acids local to specific hemes. Reorganization free energies yield a range consistent with theoretical expectations for partially solvent exposed cofactors, and reveal an activation energy range surmountable for electron flow. Quantum mechanical calculations of electronic coupling matrix elements show a clear correlation between couplings and endergonic steps of through-protein electron transfer, suggesting that the protein evolved to harbor low-potential hemes for thermodynamic range without slowing down electron flow.

Because the individual hemes are not easily distinguished spectroscopically in such proteins, none of these insights are experimentally accessible. The theory and simulation campaign on this system is thus not only enabling a fundamental advance in understanding bacterial electron transfer protein function and key design elements, but it also provides a window into the broader biogeochemical context by the evident selection pressure underlying its purpose.

Storage of Hadean oceanic crust in the Kaapvaal subcratonic mantle

G.P. BREY[1]*, Q. SHU[12], A. GERDES[1] AND H.E. HOEFER[1]

[1]Institut für Geowissenschaften, Goethe-Universität, Altenhöferallee 1, D-60438 Frankfurt, Germany (*brey@em.uni-frankfurt.de)
[2]China University of Geosciences (Beijing). Xueyuan Road 29. Haidian, Beijing, China. 100083;

Eclogites from the subcratonic lithosphere appear to be ancient and Re-Os isotope data from eclogite xenoliths from Newlands on the Kaapvaal craton suggest that some may date back to the Hadean [1]. If mantle eclogites are products of subduction of oceanic crust [2], their ages place strong constraints on the beginning of plate tectonics. The calculated bulk rock compositions of a subset of bimineralic and of kyanite and corundum bearing eclogite xenoliths from the Bellsbank diamond mine (about 30 km north of Newlands) have similar flat middle to heavy REE patterns. Their range and that of their calculated major element compositions lies within the range of modern day mid ocean ridge basalts and gabbroic rocks. The kyanite- or corundum-bearing eclogites (3 samples) display positive Eu anomalies and show depletion in the more incompatible trace elements except for an enrichment in U and Th. In accord with earlier work we interpret them as former plagioclase rich cumulates which were possibly slightly modified by dehydration during subduction and during metamorphism. We interpret the bimineralic eclogites with overall higher abundances of the more incompatible trace elements (2 samples; no Eu anomaly) as clinopyroxene-rich cumulates. Based on the chemical similarities we regard these eclogites as a cogenetic suite.

The Lu-Hf two-point isochrones from these samples with temperatures of last equilibration above 920 °C give kimberlite eruption age (= 120 Ma for Bellsbank), i.e. garnet and clinopyroxene were in continuous isotopic exchange in the mantle until the time of eruption. The reconstructed bulk rock Lu-Hf isotopic compositions of four of the five samples plot along a line in an isochron diagram which yields 4.12 ± 0.27 Ga (MSWD = 0.04) with εHf_i ~0. The reality of an Hadean age is supported by the extremely high $\varepsilon Hf_{(120Ma)}$ values up to 1004 and 1006 respectively for coexisting cpx and garnet. Further support comes from garnet model ages between 3.13-3.5 Ga. These are minimum possible ages. Values of $\delta^{18}O$ lower than the mantle (2.5‰ to 4.8‰ in garnets) are consistent with low temperature sea floor alteration as their cause. This supports the existence of oceans 4.1 Ga ago. The eclogites and their MORB-like compositions imply modern day potential mantle temperatures, at least locally, and subduction underneath microcontinents in the Hadean.

[1] Menzies *et al*., Lithos (2003); [2] Jacob, Lithos (2004)

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