

Towards the Understanding of Pressure- Induced Protein Phase Transitions

Arvi Freiberg^{1,2}, Kõu Timpmann¹, Liina Kangur¹

¹Institute of Physics, University of Tartu, W. Ostwaldi 1, 50411 Tartu, Estonia

²Estonian Academy of Sciences, Kohtu 6, 10130 Tallinn, Estonia

arvi.freiberg@ut.ee

Much of the thermodynamic parameter values that support life are set by the properties of proteins. While the denaturing effects of pressure and temperature on proteins are well documented, their detailed structural nature is rarely revealed. Here, we investigate a cooperative destabilization by hydrostatic high-pressure compression of the sixteen Ca²⁺ binding sites in the cyclic LH1 light-harvesting membrane chromoprotein complexes from calcium-containing sulfur purple bacteria. The native (Ca-saturated) and denatured (Ca-depleted) phases of the complexes are at ambient temperature clearly distinguishable from each other by much-shifted bacteriochlorophyll a exciton absorption bands, serving as innate optical probes in this study. The pressure-induced effects were found irreversible, exposing strong hysteresis in steady-state spectral properties as well as non-exponential and path-dependent pressure-jump relaxation kinetics with half-life constants shortening from tens of hours to minutes across a couple of kilobar pressure range towards compression. Our observations uniquely show a cooperative failure of the LH1 Ca-binding pockets at high pressures ($P > \sim 4$ kbar) upon compression and a cooperative reconstruction of the released into the buffer solvent Ca²⁺ ions back into the protein upon decompression at low pressures ($P < \sim 2$ kbar).