Accelerated electron transfer in nitrogenase is triggered by ATP hydrolysis

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One of the most significant bottlenecks of the nitrogen cycle is the reduction of atmospheric dinitrogen (N₂) to ammonia through the process of nitrogen fixation. Biologically, nitrogen fixation occurs through the enzyme nitrogenase and only occurs in prokaryote organisms. To facilitate reduction of N₂, nitrogenase must overcome two major barriers; the specific association of inert N₂ to a reactive centre, and reduction of the N₂ triple bond.

The nitrogenase enzyme contains an Fe₇S₉Mo-X-homocitrate cluster called FeMoco. The reduction of this cluster generates a reactive site that can associate with N₂ and sequentially reduce it to two NH₄⁺ molecules. Nitrogenase obtains electrons from a specific reductase known as the Fe protein. The Fe protein is a dimeric protein that contains a Fe₄S₄ cluster coordinated by two cysteine residues from each domain and two MgATP binding sites.

The Fe protein transfers electrons into the nitrogenase protein through a cycle that involves complex formation, ATP hydrolysis and finally complex dissociation. Using non-hydrolysable and caged ATP analogues we have investigated the role of ATP during electron transfer and shown that ATP hydrolysis, rather than complex formation, is the trigger for electron transfer between the two proteins. The ability of ATP hydrolysis to trigger electron transfer explains why the Fe protein is the only known reductant that can catalytically reduce nitrogenase.