Supplementary Information

A molecular pathway for the egress of ammonia produced by nitrogenase.

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1. The relationship between the surface terminus of the cyan pocket and the docked Fe protein was assessed for both 2AFH and 2AFI. As shown in Figure S1, the surface end of the cyan pocket is not part of the docking domain, and does not encounter the polypeptide chains of the Fe protein (blue and orange).

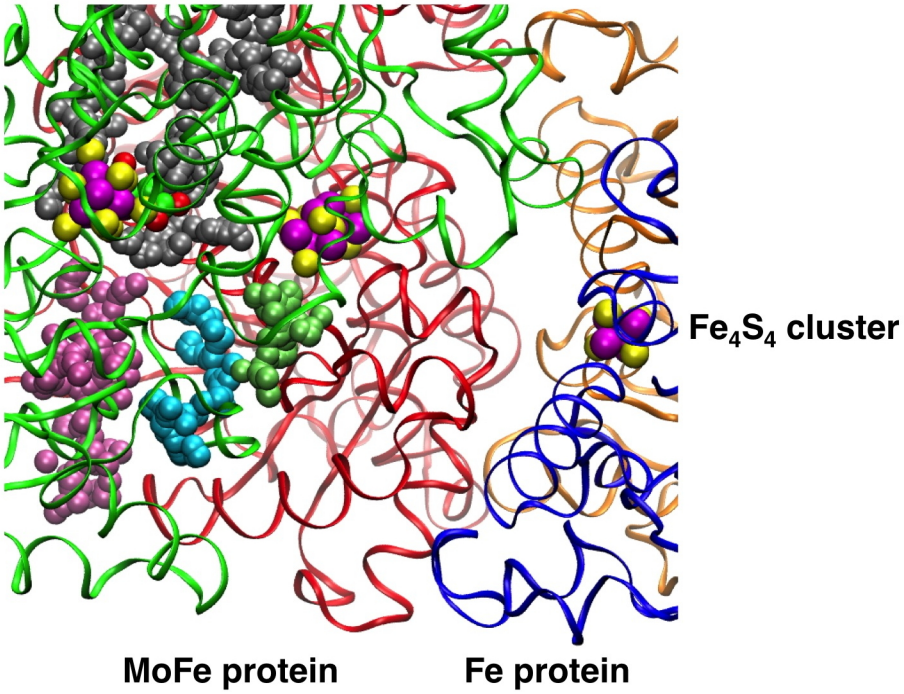

Figure S1. The docking interface of the MoFe and Fe proteins in crystal PDB 2AFH, in relation to the position of the cyan pocket and FeMo-co. The blue and orange chains comprise the Fe protein, and the green and red chains are in the MoFe protein. The electron-transfer active Fe_4S_4 cluster of the Fe protein is marked.

2. Detail of the modeled positions for hydrogen bonded NH_3 moving to and through the cyan cavity.

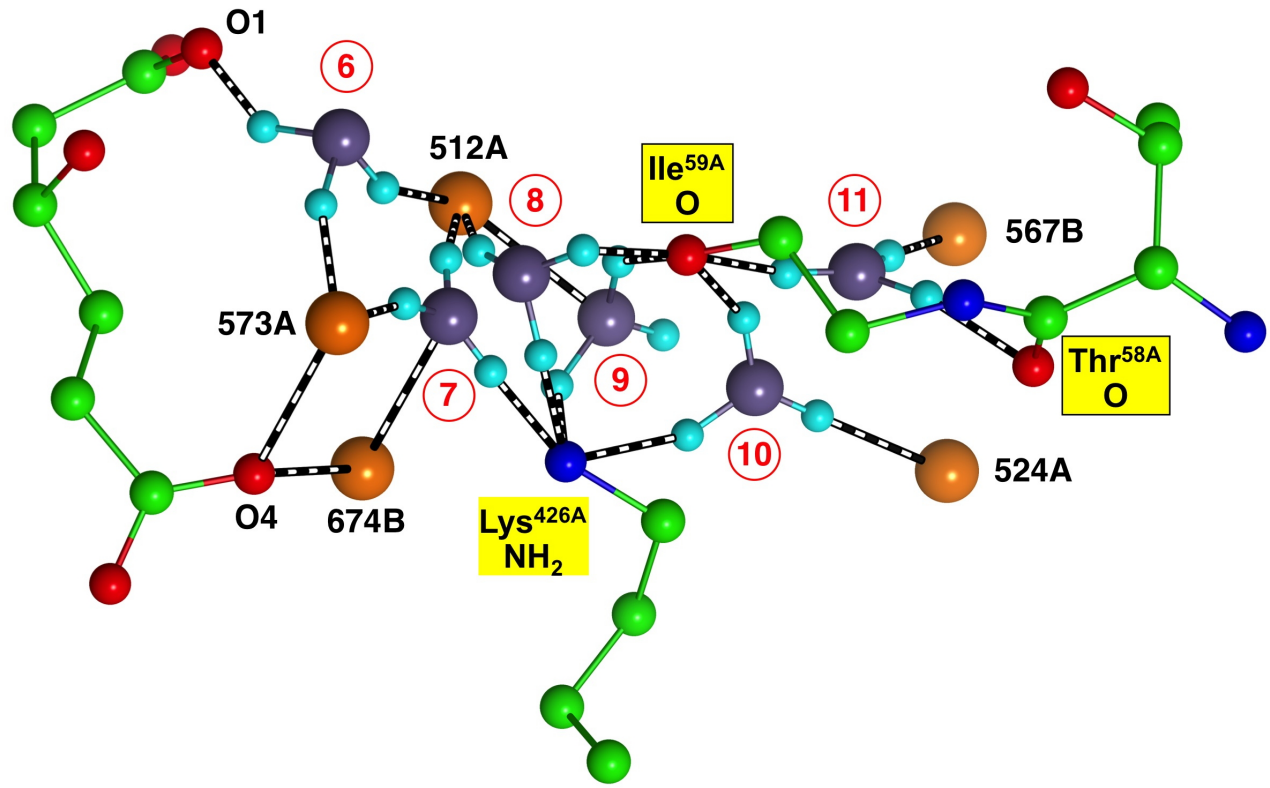

Figure S2. Sequential positions 6 to 11 of NH_3, between the water pool on the left and the beginning of the cyan cavity on the right. Homocitrate on the left is incompletely drawn.

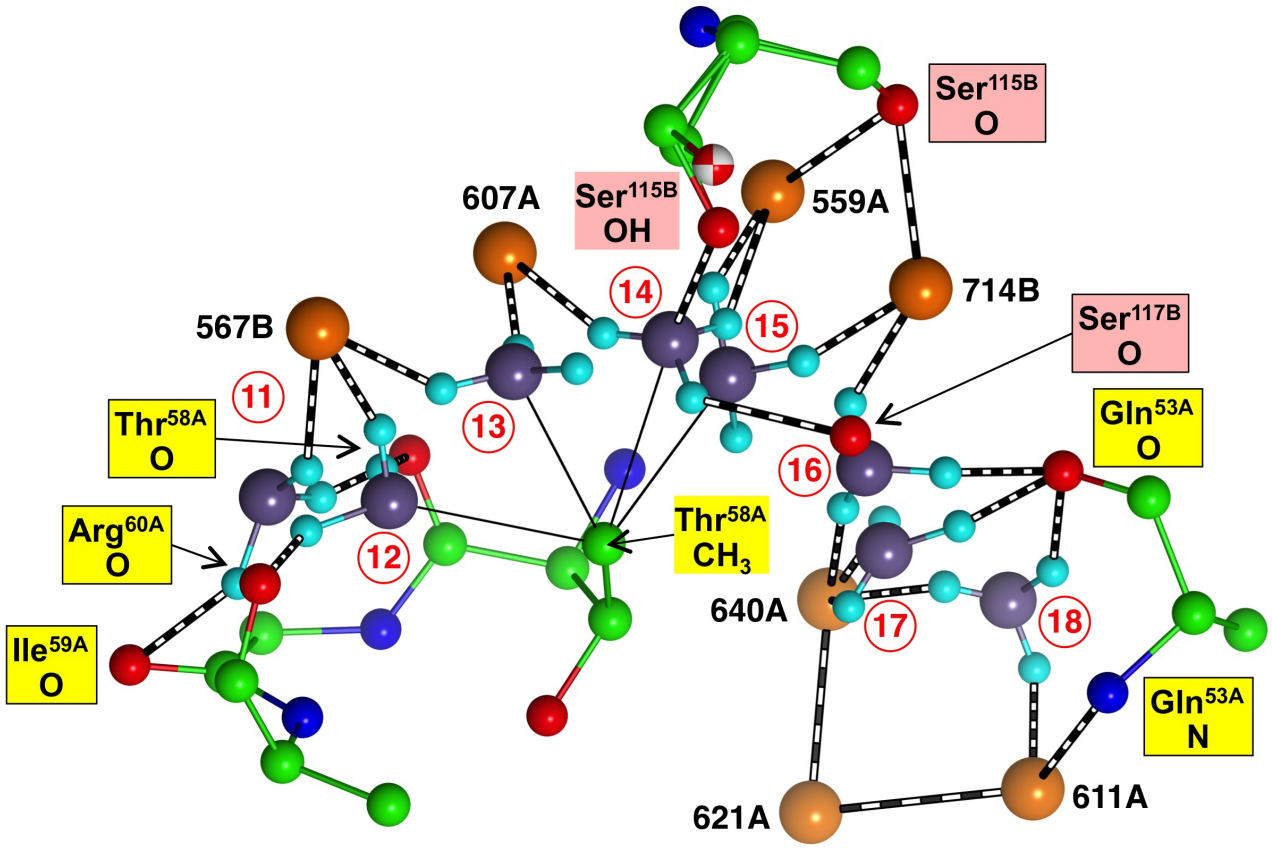

Figure S3. Positions 11 to 18 for NH_3 moving through the cyan cavity. The side chain CH_2OH function of Ser^{115B} is disordered in PDB 3U7Q and both configurations are shown (beachball and filled): only one forms a good OH → NH_3 hydrogen bond at position 14. The

lines from side chain CH_3 of Thr^{58A} are contacts of ca 2.7Å to N in positions 12, 13, 14 and 15, and are possible C-H → NH_3 hydrogen bonds.