Supporting Information

Crystallographic Trapping of Heme Loss Intermediates During the Nitrite-Induced Degradation of Human Hemoglobin

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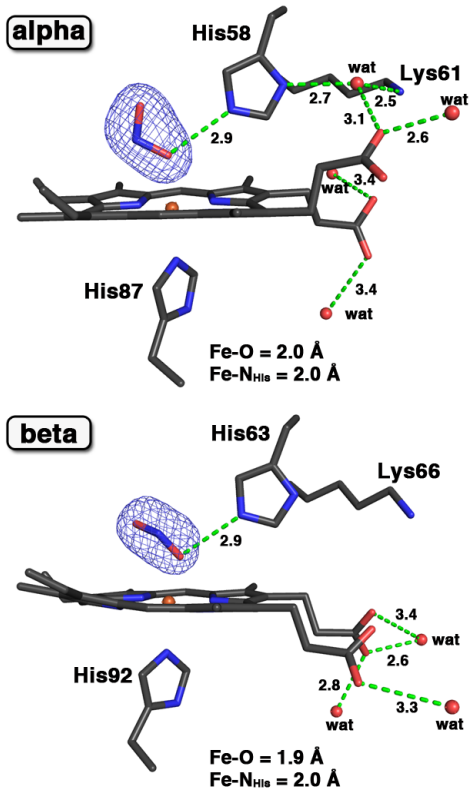

Fig. S1. F_o-F_c omit electron density map (contoured at 3.0σ) and the final model of the α- and β-heme active sites of ferric human Hb(ONO) (PDB accession code: 3D7O, 1.8 Å resolution). The H-bonding interactions are shown as green dashed lines. The F_o-F_c difference electron density maps for water molecules are not shown here. All bonds to Fe are omitted for clarity.

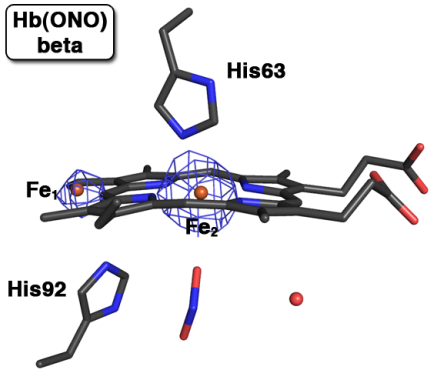

Fig. S2. The Fe anomalous map (contoured at 3.0σ) and the final model of the β heme site of the $Hb(ONO)_{d,p}$ structure (PDB accession code: 3ONZ, 2.1 Å resolution). The occupancies of Fe_1 and Fe_2 are modeled at 28% and 62%, respectively.

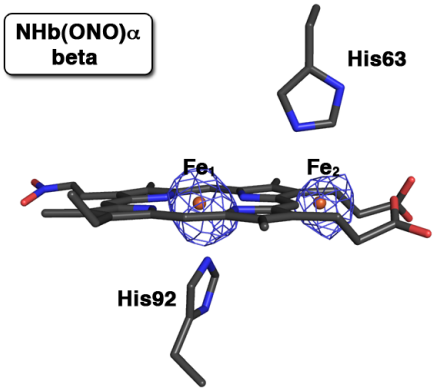

Fig. S3. The iron anomalous map (contoured at 3.0σ) and the final model of the β heme site of the NHb(ONO)α structure (PDB accession code: 3OO5, 2.1 Å resolution). The occupancies of Fe_1 and Fe_2 are modeled at 60% and 40%, respectively.

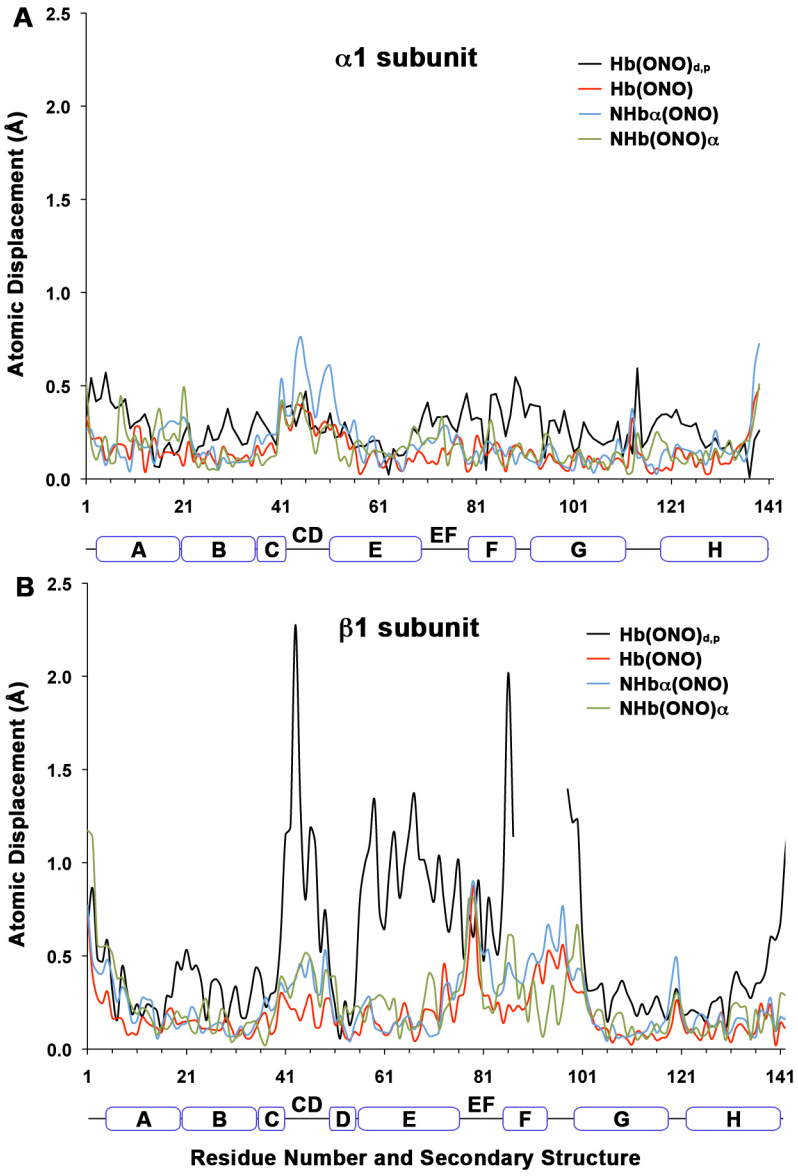

Fig. S4. Superposition of the Cα chains of four ferric *R*-state Hb nitrite structures with the Cα chain of the reference aquometHb structure (PDB accession code 3P5Q). Atomic displacements for (i) the $Hb(ONO)_{d,p}$ structure is shown in black (PDB accession code 3ONZ; 2.09 Å resolution), (ii) the Hb(ONO) structure is shown in red (PDB accession code: 3D7O, 1.8 Å resolution), (iii) the NαHb(ONO) structure is shown in blue (PDB accession code: 3OO4, 1.9 Å resolution), and (iv) the NHb(ONO)α structure is shown in green (PDB accession code: 3OO5, 2.1 Å resolution).

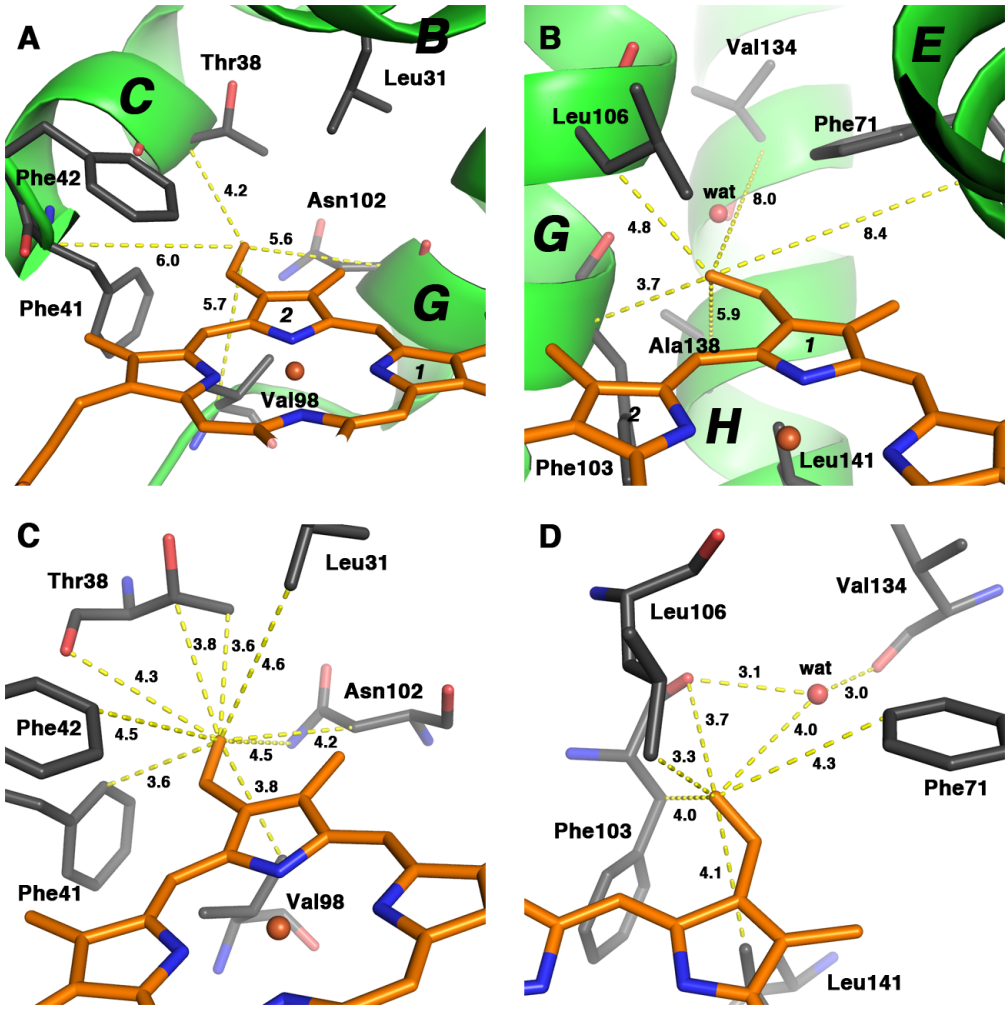

Fig. S5. The heme vinyl regions of the β subunit of ferric aquometHb (PDB accession code 3P5Q, 2.0 Å resol.). The close contacts of the terminal Cβ atoms at two vinyl positions of the β heme of the aquometHb structure with the protein backbones (Cα atoms of the nearby residues) (top panel) and the side chains of nearby residues (bottom panel) are shown as yellow dashed lines. **A**) The close contacts of the terminal Cβ atom at the 4-vinyl position with the Cα atoms of nearby helices (Helix C and Helix G); **B**) The close contacts of the terminal Cβ atom at the 2-vinyl position with the Cα atoms of nearby helices (Helix E, Helix G and Helix H); **C**) The close contacts of the terminal Cβ atom at the 4-vinyl position with the side chains of nearby residues; **D**) The close contacts of the terminal Cβ atom at the 2-vinyl position with the side chains of nearby residues.

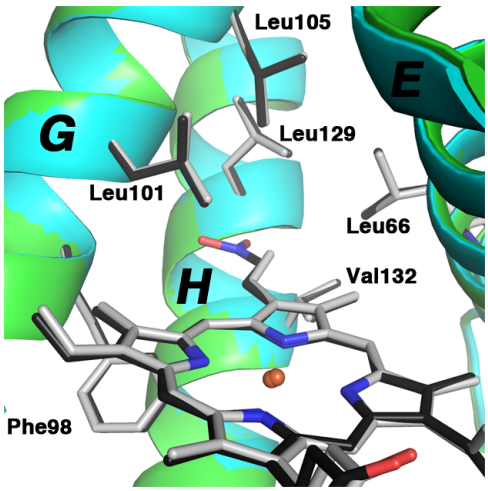

Fig. S6. The α heme sites of the superposed final models of aquometHb (PDB accession code: 3P5Q, 2.0 Å resolution) shown in green color for helices and light gray for side chains and the α heme group) and NαHb(ONO) (PDB accession code: 3OO4, 1.9 Å resol., shown in cyan color for helices and dark gray for side chains and the α heme group) structures.