

Table S1. Quality of the non-linear fitting as evaluated by residual values (%) for the derived pseudo-first-order rate constant  $k_1$ - $k_6$  for each concentration of cysteine for the reduction of MbFe(IV)=O and metMbFe(III) by cysteine at 25.0 °C and varying pH. Total residual values (%) for the derived pseudo-first-order rate constants  $k_1$ - $k_3$  (pH 6, 7, and 8) and  $k_4$ - $k_6$  (pH 9) for each [cysteine] excess. Total residual values are the residual divided by the sum of all Y-values.

[cysteine] / $10^{-3}$ mol·l <sup>-1</sup>	Residuals k1	Residuals k2	Residuals k3	Total residuals
<b>pH 6</b>				
0.94	9.93	5.88	5.28	7.32
1.57	10.4	6.21	4.91	7.42
3.14	10.3	6.65	3.74	6.19
6.29	10.4	4.43	3.40	5.41
9.43	9.98	4.60	2.99	4.87
<b>pH 7</b>				
0.94	21.3	10.2	6.61	11.7
1.57	20.6	11.1	6.78	11.5
3.14	17.4	9.51	3.52	7.17
6.30	14.9	9.94	2.44	5.17
9.43	13.1	10.1	1.69	3.79
<b>pH 8</b>				
0.94	13.0	22.0	4.73	8.67
1.57	15.9	26.1	5.25	9.34
3.14	14.2	32.7	3.87	7.56
6.30	15.3	51.7	3.76	7.33
9.43	14.8	48.9	3.27	4.41
[cysteine] / $10^{-3}$ mol·l <sup>-1</sup>	Residuals k4	Residuals k5	Residuals k6	Total residuals
<b>pH 9</b>				
0.94	4.40	1.39	46.7	2.76
1.57	5.40	1.40	39.4	2.79
3.14	3.11	1.29	24.3	2.64
6.30	2.79	0.80	8.57	1.61
9.43	2.24	1.11	2.65	1.44

Figure S1. Electronic absorption spectrum recorded at pH 7.4 in phosphate buffer (0.16 M) for **A**)  $5 \times 10^{-5} \text{ mol l}^{-1}$  of MbFe(III); **B**)  $5 \times 10^{-5} \text{ mol l}^{-1}$  of MbFe(IV)=O; and **C**) Sulfmyoglobin, spectra recorded after the reduction of  $5 \times 10^{-5} \text{ mol l}^{-1}$  of ferrylmyoglobin by excess of  $\text{H}_2\text{S}$ . **D**)  $5 \times 10^{-4} \text{ mol l}^{-1}$  of cysteine.

