

Supplemental Table 1. List of Proteins with Detected Cysteine-SOH Modifications (excluding those identified in proteomic screens). Each referenced entry indicates the species, particular cysteine residue modified (if known), oxidative treatment that accompanied detection and the methodology employed.

Protein Name	Species	Cysteine	Detection Method(s) [#]	Oxidant Treatment(s)	Reference
1-Cys OxyR	<i>D. radiodurans</i>	210	N	cumene-hydroperoxide	(1)
1-Cys Prx	<i>B. taurus</i>		T	hydrogen peroxide, peroxyxynitrite	(2)
20S Proteasome	<i>S. cerevisiae</i>		N	hydrogen peroxide	(3)
20S Proteasome	<i>S. cerevisiae</i>		N	hydrogen peroxide	(4)
Actin	<i>H. sapiens</i>		D	hydrogen peroxide	(5)
Actin	<i>H. sapiens</i>		D, SR	no treatment	(6)
Actin	<i>R. norvegicus</i>	217	MS, SR	no treatment, x-ray irradiation	(7)
Alcohol Dehydrogenase	<i>S. cerevisiae</i>		DR	hydrogen peroxide	(8)
AhpC (C165S)	<i>S. typhimurium</i>	46	N	peroxyxynitrite	(9)
AhpC (C165S)	<i>S. typhimurium</i>	46	N	hydrogen peroxide	(10)
AhpC (C165S)	<i>S. typhimurium</i>	46	T	hydrogen peroxide	(11)
AhpC (C165S)	<i>S. typhimurium</i>	46	DR	hydrogen peroxide	(12)
AhpC (C165S)	<i>S. typhimurium</i>	46	DR	hydrogen peroxide	(13)
AhpE	<i>M. tuberculosis</i>	45	T	hydrogen peroxide	(14)
AhpE	<i>M. tuberculosis</i>	45	X	no treatment	(15)
Akt1	<i>H. sapiens</i>	310	MS	no treatment, hydrogen peroxide	(16)
Albumin	<i>B. taurus</i>	34	SR	hydrogen peroxide	(17)
Albumin	<i>B. taurus</i>	34	SR	hydrogen peroxide, xanthine oxidase	(18)
Albumin	<i>H. sapiens</i>	34	DR	hydrogen peroxide	(8)
Albumin	<i>H. sapiens</i>	34	D	nitric oxide (anaerobic)	(19)
Albumin	<i>B. taurus</i>	34	N	hydrogen peroxide + bicarbonate	(20)
Albumin	<i>B. taurus</i>	34	N	hydrogen peroxide + nitrite, hydrogen peroxide + bicarbonate	(21)
Albumin	<i>H. sapiens</i>	34	N	taurine chloramine	(22)
Albumin	<i>H. sapiens</i>	34	T	hydrogen peroxide	(23)
Albumin	<i>H. sapiens</i>	34	N, D	hydrogen peroxide, peroxyxynitrite	(24)
Aldose Reductase	<i>H. sapiens</i>	298	D	peroxyxynitrite	(25)

Aldose Reductase	<i>H. sapiens</i>	298, 303	D	hydrogen peroxide	(26)
Aldose Reductase	<i>R. norvegicus</i>	80, 92, 298, 303	D, MS	ischemia	(26)
Alpha1 Antitrypsin	<i>H. sapiens</i>	232	N	hydrogen peroxide	(27)
Arylamine N-acetyltransferase	<i>H. sapiens</i>	68	D	hydrogen peroxide	(28)
Bacterioferritin Comigratory Protein (C50S)	<i>E. coli</i>	45	N	hydrogen peroxide	(29)
Bacterioferritin Comigratory Protein	<i>E. coli</i>	45	N	no treatment	(30)
Betaine Aldehyde Dehydrogenase	<i>P. aeruginosa</i>	286	X	no treatment	(31)
Calreticulin	<i>H. sapiens</i>		DR	no treatment	(32)
Cathepsin K	<i>H. sapiens</i>	25	D	NOR-1 (nitric oxide donor)	(33)
CDC25B Phosphatase (C426S)	<i>H. sapiens</i>	473	MS	hydrogen peroxide	(34)
Cytosolic Branched Chain Aminotransferase	<i>H. sapiens</i>	335	D	hydrogen peroxide	(35)
Formylglycine Generating Enzyme	<i>H. sapiens</i>	336	X	no treatment	(36)
Glutathione Reductase	<i>H. sapiens</i>	63	X	S-nitrosoglutathione	(37)
Glutathione S Transferase (microsomal)	<i>R. norvegicus</i>	49	SR	peroxynitrite	(38)
Glutathione S Transferase (mitochondrial)	<i>R. norvegicus</i>		SR	gallic acid	(39)
GAPDH	<i>O. cuniculus</i>	149	BA	o-iodosobenzoate	(40)
GAPDH	<i>S. domestica</i>	149	D, DR	o-iodosobenzoate	(41)
GAPDH	<i>O. cuniculus</i>	149	SR	hydrogen peroxide	(42)
GAPDH	<i>S. domestica</i>	149	SR	o-iodosobenzoate, iodine monochloride	(43)
GAPDH (C153S)	<i>B. stearothermophilus</i>	149	SR	hydrogen peroxide	(44)
GAPDH	<i>S. domestica</i>	149	SR	trinitroglycerin	(45)
GAPDH	<i>H. sapiens</i>		DR	no treatment, hydrogen peroxide	(32)
GAPDH	<i>O. cuniculus</i>	149	D	hydrogen peroxide	(5)
GAPDH	<i>H. sapiens</i>	152	D	hydrogen peroxide	(5)
Gpx3/Orp1	<i>S. cerevisiae</i>	36	DR	hydrogen peroxide	(46)
Gpx3/Orp1 (C64S,C82S)	<i>S. cerevisiae</i>	36	N	hydrogen peroxide	(47)
Hemoglobin (beta chain)	<i>H. sapiens</i>	93	D, MS	hydrogen peroxide	(48)
hORF6	<i>H. sapiens</i>	47	X	no treatment	(49)

IgG1	<i>H. sapiens</i>	231	MS	hydrogen peroxide	(50)
Ikappa B Kinase (beta subunit)	<i>M. musculus</i>	179	D	hydrogen peroxide	(51)
Malate Synthase G	<i>E. coli</i>	617	X	no treatment	(52)
Methionine Sulfoxide Reductase A (C86S,C198S,C206S)	<i>E. coli</i>	51	T	hydrogen peroxide, methionine sulfoxide	(53)
Methionine Sulfoxide Reductase A (C198S)	<i>N. meningitis</i>	51	X	no treatment	(54)
Methionine Sulfoxide Reductase B	<i>D. melanogaster</i>	124	D	methionine sulfoxide	(55)
Methionine Sulfoxide Reductase B (C31S)	<i>X. campestris</i>	117	T	no treatment	(56)
Methionine Sulfoxide Reductase B1	<i>A. thaliana</i>	186	MS	methionine sulfoxide	(57)
Mitochondrial Branched Chain Aminotransferase (C318A)	<i>H. sapiens</i>	315	MS, D	hydrogen peroxide	(58)
Mitochondrial 1-Cys Prx	<i>S. cerevisiae</i>	91	MS	hydrogen peroxide	(59)
MKP-3 (C287S,C309S)	<i>H. sapiens</i>	293	MS	hydrogen peroxide	(60)
NADPH Oxidase	<i>L. sanfranciscensis</i>	42	X	no treatment	(61)
NADH peroxidase	<i>E. faecalis</i>	42	NMR	no treatment	(62)
NADH peroxidase	<i>S. faecalis</i>	42	T	no treatment	(63)
NADH peroxidase	<i>E. faecalis</i>	42	X	no treatment	(64)
NADH peroxidase	<i>S. faecalis</i>	42	X	no treatment	(65)
Nitrile Hydratase	<i>P. thermophilia</i>	113	X	no treatment	(66)
OhrR (C127S,C131S)	<i>X. campestris</i>	22	N	cumene-hydroperoxide	(67)
OhrR	<i>B. subtilis</i>	15	N, MS	cumene-hydroperoxide	(68)
OxyR	<i>E. coli</i>	199	N	hydrogen peroxide	(69)
NF-kappaB (p50 subunit)	<i>H. sapiens</i>	62	D	hydrogen peroxide	(70)
Papain	<i>C. papaya</i>	25	SR, T	hydrogen peroxide	(71)
Papain	<i>C. papaya</i>	25	DR	hydrogen peroxide	(8)
Papain	<i>C. papaya</i>	25	DR	hydrogen peroxide	(13)
Papain	<i>C. papaya</i>	25	D	hydrogen peroxide	(5)
Papain	<i>C. papaya</i>	25	N	hydrogen peroxide, tryptophan-hydroperoxide	(72)
PAPS reductase	<i>E. coli</i>		DR	hydrogen peroxide	(8)
PILB (C348S)	<i>N. meningitis</i>	206	T, D	methionine sulfoxide	(73)

Prx	<i>A. pernix</i>	50	X	no treatment	(74)
Prx1	<i>H. sapiens</i>		DR	hydrogen peroxide	(32)
Prx1	<i>H. sapiens</i>		D	hydrogen peroxide	(5)
Prx1	<i>S. cerevisiae</i>		D	hydrogen peroxide	(75)
Protein Tyrosine Phosphatase 1B	<i>H. sapiens</i>	215	X	no treatment	(76)
Rab1a	<i>H. sapiens</i>	26, 126	DR	hydrogen peroxide	(32)
S100A8	<i>M. musculus</i>	41	MD, D	hypochlorous acid	(77)
SarZ	<i>S. aureus</i>	13	N, X	cumene-hydroperoxide	(78)
S-Formylglutathione Hydrolase	<i>S. cerevisiae</i>	60	X	no treatment	(79)
Shp1	<i>M. musculus</i>	453	DR	phorbol myristate acetate + ionomycin	(80)
Shp2	<i>M. musculus</i>	459	DR	phorbol myristate acetate + ionomycin	(80)
Sortase A	<i>S. pyogenes</i>	208	X	no treatment	(81)
Tetrachlorohydroquinone Dehalogenase	<i>S. chlorophenolicus</i>	13	D	hydrogen peroxide	(82)
Thiocyanate Hydrolase	<i>E. coli</i>	133	X	no treatment	(83)
Thiocyanate Hydrolase	<i>T. thioparus</i>	133	X	no treatment	(84)
Thiol Peroxidase (C82S,C95S)	<i>E. coli</i>	61	N	cumene-hydroperoxide	(85)
Tsa1 (C170S)	<i>S. cerevisiae</i>		N	hydrogen peroxide	(75)
Ulp1	<i>S. cerevisiae</i>	580	X	no treatment	(86)
Vaccinia H1-Related Protein	<i>H. sapiens</i>	124	N	hydrogen peroxide	(87)
YajL	<i>E. coli</i>	106	X	no treatment	(88)
YbiS	<i>E. coli</i>	186	DR	no treatment, hydrogen peroxide	(89)
YhaK	<i>E. coli</i>	122	X	no treatment	(90)

Legend for Detection Methodology: N = 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl), T = 5-thio-2-nitrobenzoate (TNB), D = 5,5-dimethyl-1,3-cyclohexanedione (Dimedone), SR = Selective Reduction, MS = Direct Mass Spectrometry, DR = Dimedone Derivatives, X = X-ray Crystal Structure, NMR = ¹³C NMR, BA = benzylamine.

References

1. Chen, H., Xu, G., Zhao, Y., Tian, B., Lu, H., Yu, X., Xu, Z., Ying, N., Hu, S., and Hua, Y. (2008) A novel OxyR sensor and regulator of hydrogen peroxide stress with one cysteine residue in *Deinococcus radiodurans*, *PLoS One* 3, e1602.
2. Peshenko, I. V., and Shichi, H. (2001) Oxidation of active center cysteine of bovine 1-Cys peroxiredoxin to the cysteine sulfenic acid form by peroxide and peroxynitrite, *Free Radic Biol Med* 31, 292-303.
3. Demasi, M., Silva, G. M., and Netto, L. E. (2003) 20 S proteasome from *Saccharomyces cerevisiae* is responsive to redox modifications and is S-glutathionylated, *J Biol Chem* 278, 679-685.
4. Silva, G. M., Netto, L. E., Discola, K. F., Piassa-Filho, G. M., Pimenta, D. C., Barcena, J. A., and Demasi, M. (2008) Role of glutaredoxin 2 and cytosolic thioredoxins in cysteinyl-based redox modification of the 20S proteasome, *FEBS J* 275, 2942-2955.
5. Seo, Y. H., and Carroll, K. S. (2009) Profiling protein thiol oxidation in tumor cells using sulfenic acid-specific antibodies, *Proc Natl Acad Sci U S A* 106, 16163-16168.
6. Johansson, M., and Lundberg, M. (2007) Glutathionylation of beta-actin via a cysteinyl sulfenic acid intermediary, *BMC Biochem* 8, 26.
7. Fedorova, M., Kuleva, N., and Hoffmann, R. (2010) Identification of cysteine, methionine and tryptophan residues of actin oxidized in vivo during oxidative stress, *J Proteome Res* 9, 1598-1609.
8. Reddie, K. G., Seo, Y. H., Muse Iii, W. B., Leonard, S. E., and Carroll, K. S. (2008) A chemical approach for detecting sulfenic acid-modified proteins in living cells, *Mol Biosyst* 4, 521-531.
9. Bryk, R., Griffin, P., and Nathan, C. (2000) Peroxynitrite reductase activity of bacterial peroxiredoxins, *Nature* 407, 211-215.
10. Ellis, H. R., and Poole, L. B. (1997) Novel application of 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole to identify cysteine sulfenic acid in the AhpC component of alkyl hydroperoxide reductase, *Biochemistry* 36, 15013-15018.
11. Ellis, H. R., and Poole, L. B. (1997) Roles for the two cysteine residues of AhpC in catalysis of peroxide reduction by alkyl hydroperoxide reductase from *Salmonella typhimurium*, *Biochemistry* 36, 13349-13356.
12. Poole, L. B., Zeng, B. B., Knaggs, S. A., Yakubu, M., and King, S. B. (2005) Synthesis of chemical probes to map sulfenic acid modifications on proteins, *Bioconjug Chem* 16, 1624-1628.
13. Poole, L. B., Klomsiri, C., Knaggs, S. A., Furdui, C. M., Nelson, K. J., Thomas, M. J., Fetrow, J. S., Daniel, L. W., and King, S. B. (2007) Fluorescent and affinity-based tools to detect cysteine sulfenic acid formation in proteins, *Bioconjug Chem* 18, 2004-2017.
14. Hugo, M., Turell, L., Manta, B., Botti, H., Monteiro, G., Netto, L. E., Alvarez, B., Radi, R., and Trujillo, M. (2009) Thiol and sulfenic acid oxidation of AhpE, the one-cysteine peroxiredoxin from *Mycobacterium tuberculosis*: kinetics, acidity constants, and conformational dynamics, *Biochemistry* 48, 9416-9426.

15. Li, S., Peterson, N. A., Kim, M. Y., Kim, C. Y., Hung, L. W., Yu, M., Lakin, T., Segelke, B. W., Lott, J. S., and Baker, E. N. (2005) Crystal Structure of AhpE from *Mycobacterium tuberculosis*, a 1-Cys peroxiredoxin, *J Mol Biol* 346, 1035-1046.
16. Antico Arciuch, V. G., Galli, S., Franco, M. C., Lam, P. Y., Cadenas, E., Carreras, M. C., and Poderoso, J. J. (2009) Akt1 intramitochondrial cycling is a crucial step in the redox modulation of cell cycle progression, *PLoS One* 4, e7523.
17. Radi, R., Beckman, J. S., Bush, K. M., and Freeman, B. A. (1991) Peroxynitrite oxidation of sulfhydryls. The cytotoxic potential of superoxide and nitric oxide, *J Biol Chem* 266, 4244-4250.
18. Radi, R., Bush, K. M., Cosgrove, T. P., and Freeman, B. A. (1991) Reaction of xanthine oxidase-derived oxidants with lipid and protein of human plasma, *Arch Biochem Biophys* 286, 117-125.
19. DeMaster, E. G., Quast, B. J., Redfern, B., and Nagasawa, H. T. (1995) Reaction of nitric oxide with the free sulfhydryl group of human serum albumin yields a sulfenic acid and nitrous oxide, *Biochemistry* 34, 11494-11499.
20. Trindade, D. F., Cerchiaro, G., and Augusto, O. (2006) A role for peroxymonocarbonate in the stimulation of biothiol peroxidation by the bicarbonate/carbon dioxide pair, *Chem Res Toxicol* 19, 1475-1482.
21. Bonini, M. G., Fernandes, D. C., and Augusto, O. (2004) Albumin oxidation to diverse radicals by the peroxidase activity of Cu,Zn-superoxide dismutase in the presence of bicarbonate or nitrite: diffusible radicals produce cysteinyl and solvent-exposed and -unexposed tyrosyl radicals, *Biochemistry* 43, 344-351.
22. Peskin, A. V., and Winterbourn, C. C. (2006) Taurine chloramine is more selective than hypochlorous acid at targeting critical cysteines and inactivating creatine kinase and glyceraldehyde-3-phosphate dehydrogenase, *Free Radic Biol Med* 40, 45-53.
23. Turell, L., Botti, H., Carballal, S., Ferrer-Sueta, G., Souza, J. M., Duran, R., Freeman, B. A., Radi, R., and Alvarez, B. (2008) Reactivity of sulfenic acid in human serum albumin, *Biochemistry* 47, 358-367.
24. Carballal, S., Radi, R., Kirk, M. C., Barnes, S., Freeman, B. A., and Alvarez, B. (2003) Sulfenic acid formation in human serum albumin by hydrogen peroxide and peroxynitrite, *Biochemistry* 42, 9906-9914.
25. Kaiserova, K., Tang, X. L., Srivastava, S., and Bhatnagar, A. (2008) Role of nitric oxide in regulating aldose reductase activation in the ischemic heart, *J Biol Chem* 283, 9101-9112.
26. Kaiserova, K., Srivastava, S., Hoetker, J. D., Awe, S. O., Tang, X. L., Cai, J., and Bhatnagar, A. (2006) Redox activation of aldose reductase in the ischemic heart, *J Biol Chem* 281, 15110-15120.
27. Griffiths, S. W., King, J., and Cooney, C. L. (2002) The reactivity and oxidation pathway of cysteine 232 in recombinant human alpha 1-antitrypsin, *J Biol Chem* 277, 25486-25492.
28. Atmane, N., Dairou, J., Paul, A., Dupret, J. M., and Rodrigues-Lima, F. (2003) Redox regulation of the human xenobiotic metabolizing enzyme arylamine N-acetyltransferase 1 (NAT1). Reversible inactivation by hydrogen peroxide, *J Biol Chem* 278, 35086-35092.

29. Clarke, D. J., Mackay, C. L., Campopiano, D. J., Langridge-Smith, P., and Brown, A. R. (2009) Interrogating the molecular details of the peroxiredoxin activity of the Escherichia coli bacterioferritin comigratory protein using high-resolution mass spectrometry, *Biochemistry* 48, 3904-3914.
30. Jeong, W., Cha, M. K., and Kim, I. H. (2000) Thioredoxin-dependent hydroperoxide peroxidase activity of bacterioferritin comigratory protein (BCP) as a new member of the thiol-specific antioxidant protein (TSA)/Alkyl hydroperoxide peroxidase C (AhpC) family, *J Biol Chem* 275, 2924-2930.
31. Gonzalez-Segura, L., Rudino-Pinera, E., Munoz-Clares, R. A., and Horjales, E. (2009) The crystal structure of a ternary complex of betaine aldehyde dehydrogenase from Pseudomonas aeruginosa Provides new insight into the reaction mechanism and shows a novel binding mode of the 2'-phosphate of NADP+ and a novel cation binding site, *J Mol Biol* 385, 542-557.
32. Leonard, S. E., Reddie, K. G., and Carroll, K. S. (2009) Mining the thiol proteome for sulfenic acid modifications reveals new targets for oxidation in cells, *ACS Chem Biol* 4, 783-799.
33. Percival, M. D., Ouellet, M., Campagnolo, C., Claveau, D., and Li, C. (1999) Inhibition of cathepsin K by nitric oxide donors: evidence for the formation of mixed disulfides and a sulfenic acid, *Biochemistry* 38, 13574-13583.
34. Sohn, J., and Rudolph, J. (2003) Catalytic and chemical competence of regulation of cdc25 phosphatase by oxidation/reduction, *Biochemistry* 42, 10060-10070.
35. Conway, M. E., Coles, S. J., Islam, M. M., and Hutson, S. M. (2008) Regulatory control of human cytosolic branched-chain aminotransferase by oxidation and S-glutathionylation and its interactions with redox sensitive neuronal proteins, *Biochemistry* 47, 5465-5479.
36. Dierks, T., Dickmanns, A., Preusser-Kunze, A., Schmidt, B., Mariappan, M., von Figura, K., Ficner, R., and Rudolph, M. G. (2005) Molecular basis for multiple sulfatase deficiency and mechanism for formylglycine generation of the human formylglycine-generating enzyme, *Cell* 121, 541-552.
37. Becker, K., Savvides, S. N., Keese, M., Schirmer, R. H., and Karplus, P. A. (1998) Enzyme inactivation through sulfhydryl oxidation by physiologic NO-carriers, *Nat Struct Biol* 5, 267-271.
38. Imaizumi, N., Miyagi, S., and Aniya, Y. (2006) Reactive nitrogen species derived activation of rat liver microsomal glutathione S-transferase, *Life Sci* 78, 2998-3006.
39. Shinno, E., Shimoji, M., Imaizumi, N., Kinoshita, S., Sunakawa, H., and Aniya, Y. (2005) Activation of rat liver microsomal glutathione S-transferase by gallic acid, *Life Sci* 78, 99-106.
40. Allison, W. S., Benitez, L. V., and Johnson, C. L. (1973) The formation of a protein sulfenamide during the inactivation of the acyl phosphatase activity of oxidized glyceraldehyde-3-phosphate dehydrogenase by benzylamine, *Biochem Biophys Res Commun* 52, 1403-1409.

41. Benitez, L. V., and Allison, W. S. (1974) The inactivation of the acyl phosphatase activity catalyzed by the sulfenic acid form of glyceraldehyde 3-phosphate dehydrogenase by dimedone and olefins, *J Biol Chem* 249, 6234-6243.
42. Little, C., and O'Brien, P. J. (1969) Mechanism of peroxide-inactivation of the sulphhydryl enzyme glyceraldehyde-3-phosphate dehydrogenase, *Eur J Biochem* 10, 533-538.
43. Parker, D. J., and Allison, W. S. (1969) The mechanism of inactivation of glyceraldehyde 3-phosphate dehydrogenase by tetrathionate, o-iodosobenzoate, and iodine monochloride, *J Biol Chem* 244, 180-189.
44. Schmalhausen, E. V., Nagradova, N. K., Boschi-Muller, S., Branlant, G., and Mironetz, V. I. (1999) Mildly oxidized GAPDH: the coupling of the dehydrogenase and acyl phosphatase activities, *FEBS Lett* 452, 219-222.
45. You, K. S., Benitez, L. V., McConachie, W. A., and Allison, W. S. (1975) The conversion of glyceraldehyde-3-phosphate dehydrogenase to an acylphosphatase by trinitroglycerin and inactivation of this activity by azide and ascorbate., *Biochim Biophys Acta* 384, 317-330.
46. Paulsen, C. E., and Carroll, K. S. (2009) Chemical dissection of an essential redox switch in yeast, *Chem Biol* 16, 217-225.
47. Ma, L. H., Takanishi, C. L., and Wood, M. J. (2007) Molecular mechanism of oxidative stress perception by the Orp1 protein, *J Biol Chem* 282, 31429-31436.
48. Regazzoni, L., Panusa, A., Yeum, K. J., Carini, M., and Aldini, G. (2009) Hemoglobin glutathionylation can occur through cysteine sulfenic acid intermediate: electrospray ionization LTQ-Orbitrap hybrid mass spectrometry studies, *J Chromatogr B Analyt Technol Biomed Life Sci* 877, 3456-3461.
49. Choi, H. J., Kang, S. W., Yang, C. H., Rhee, S. G., and Ryu, S. E. (1998) Crystal structure of a novel human peroxidase enzyme at 2.0 Å resolution, *Nat Struct Biol* 5, 400-406.
50. Yan, B., Yates, Z., Balland, A., and Kleemann, G. R. (2009) Human IgG1 hinge fragmentation as the result of H₂O₂-mediated radical cleavage, *J Biol Chem* 284, 35390-35402.
51. Reynaert, N. L., van der Vliet, A., Guala, A. S., McGovern, T., Hristova, M., Pantano, C., Heintz, N. H., Heim, J., Ho, Y. S., Matthews, D. E., Wouters, E. F., and Janssen-Heininger, Y. M. (2006) Dynamic redox control of NF- κ B through glutaredoxin-regulated S-glutathionylation of inhibitory κ B kinase beta, *Proc Natl Acad Sci U S A* 103, 13086-13091.
52. Anstrom, D. M., Kallio, K., and Remington, S. J. (2003) Structure of the Escherichia coli malate synthase G:pyruvate:acetyl-coenzyme A abortive ternary complex at 1.95 Å resolution, *Protein Sci* 12, 1822-1832.
53. Boschi-Muller, S., Azza, S., Sanglier-Cianferani, S., Talfournier, F., Van Dorsselaar, A., and Branlant, G. (2000) A sulfenic acid enzyme intermediate is involved in the catalytic mechanism of peptide methionine sulfoxide reductase from Escherichia coli, *J Biol Chem* 275, 35908-35913.
54. Ranaivoson, F. M., Antoine, M., Kauffmann, B., Boschi-Muller, S., Aubry, A., Branlant, G., and Favier, F. (2008) A structural analysis of the catalytic mechanism of methionine sulfoxide reductase A from Neisseria meningitidis, *J Mol Biol* 377, 268-280.

55. Kumar, R. A., Koc, A., Cerny, R. L., and Gladyshev, V. N. (2002) Reaction mechanism, evolutionary analysis, and role of zinc in *Drosophila* methionine-S-adenosylmethionine reductase, *J Biol Chem* 277, 37527-37535.
56. Neiers, F., Kriznik, A., Boschi-Muller, S., and Branlant, G. (2004) Evidence for a new sub-class of methionine sulfoxide reductases B with an alternative thioredoxin recognition signature, *J Biol Chem* 279, 42462-42468.
57. Tarrago, L., Laugier, E., Zaffagnini, M., Marchand, C., Le Marechal, P., Rouhier, N., Lemaire, S. D., and Rey, P. (2009) Regeneration mechanisms of *Arabidopsis thaliana* methionine sulfoxide reductases B by glutaredoxins and thioredoxins, *J Biol Chem* 284, 18963-18971.
58. Conway, M. E., Poole, L. B., and Hutson, S. M. (2004) Roles for cysteine residues in the regulatory CXXC motif of human mitochondrial branched chain aminotransferase enzyme, *Biochemistry* 43, 7356-7364.
59. Greetham, D., and Grant, C. M. (2009) Antioxidant activity of the yeast mitochondrial one-Cys peroxiredoxin is dependent on thioredoxin reductase and glutathione in vivo, *Mol Cell Biol* 29, 3229-3240.
60. Kamata, H., Honda, S., Maeda, S., Chang, L., Hirata, H., and Karin, M. (2005) Reactive oxygen species promote TNF α -induced death and sustained JNK activation by inhibiting MAP kinase phosphatases, *Cell* 120, 649-661.
61. Lountos, G. T., Jiang, R., Wellborn, W. B., Thaler, T. L., Bommarius, A. S., and Orville, A. M. (2006) The crystal structure of NAD(P)H oxidase from *Lactobacillus sanfranciscensis*: insights into the conversion of O₂ into two water molecules by the flavoenzyme, *Biochemistry* 45, 9648-9659.
62. Crane, E. J., 3rd, Vervoort, J., and Claiborne, A. (1997) ¹³C NMR analysis of the cysteine-sulfenic acid redox center of enterococcal NADH peroxidase, *Biochemistry* 36, 8611-8618.
63. Poole, L. B., and Claiborne, A. (1989) The non-flavin redox center of the streptococcal NADH peroxidase. II. Evidence for a stabilized cysteine-sulfenic acid, *J Biol Chem* 264, 12330-12338.
64. Yeh, J. I., Claiborne, A., and Hol, W. G. (1996) Structure of the native cysteine-sulfenic acid redox center of enterococcal NADH peroxidase refined at 2.8 Å resolution, *Biochemistry* 35, 9951-9957.
65. Stehle, T., Ahmed, S. A., Claiborne, A., and Schulz, G. E. (1990) The structure of NADH peroxidase from *Streptococcus faecalis* at 3.3 Å resolution, *FEBS Lett* 267, 186-188.
66. Miyanaga, A., Fushinobu, S., Ito, K., and Wakagi, T. (2001) Crystal structure of cobalt-containing nitrile hydratase, *Biochem Biophys Res Commun* 288, 1169-1174.
67. Panmanee, W., Vattanaviboon, P., Poole, L. B., and Mongkolsuk, S. (2006) Novel organic hydroperoxide-sensing and responding mechanisms for OhrR, a major bacterial sensor and regulator of organic hydroperoxide stress, *J Bacteriol* 188, 1389-1395.
68. Fuangthong, M., and Helmann, J. D. (2002) The OhrR repressor senses organic hydroperoxides by reversible formation of a cysteine-sulfenic acid derivative, *Proc Natl Acad Sci U S A* 99, 6690-6695.

69. Lee, C., Lee, S. M., Mukhopadhyay, P., Kim, S. J., Lee, S. C., Ahn, W. S., Yu, M. H., Storz, G., and Ryu, S. E. (2004) Redox regulation of OxyR requires specific disulfide bond formation involving a rapid kinetic reaction path, *Nat Struct Mol Biol* 11, 1179-1185.
70. Pineda-Molina, E., Klatt, P., Vazquez, J., Marina, A., Garcia de Lacoba, M., Perez-Sala, D., and Lamas, S. (2001) Glutathionylation of the p50 subunit of NF-kappaB: a mechanism for redox-induced inhibition of DNA binding, *Biochemistry* 40, 14134-14142.
71. Lin, W. S., Armstrong, D. A., and Gaucher, G. M. (1975) Formation and repair of papain sulfenic acid, *Can J Biochem* 53, 298-307.
72. Headlam, H. A., Gracanin, M., Rodgers, K. J., and Davies, M. J. (2006) Inhibition of cathepsins and related proteases by amino acid, peptide, and protein hydroperoxides, *Free Radic Biol Med* 40, 1539-1548.
73. Olry, A., Boschi-Muller, S., Marraud, M., Sanglier-Cianferani, S., Van Dorsselear, A., and Branlant, G. (2002) Characterization of the methionine sulfoxide reductase activities of PILB, a probable virulence factor from *Neisseria meningitidis*, *J Biol Chem* 277, 12016-12022.
74. Nakamura, T., Yamamoto, T., Abe, M., Matsumura, H., Hagihara, Y., Goto, T., Yamaguchi, T., and Inoue, T. (2008) Oxidation of archaeal peroxiredoxin involves a hypervalent sulfur intermediate, *Proc Natl Acad Sci U S A* 105, 6238-6242.
75. Monteiro, G., Horta, B. B., Pimenta, D. C., Augusto, O., and Netto, L. E. (2007) Reduction of 1-Cys peroxiredoxins by ascorbate changes the thiol-specific antioxidant paradigm, revealing another function of vitamin C, *Proc Natl Acad Sci U S A* 104, 4886-4891.
76. van Montfort, R. L., Congreve, M., Tisi, D., Carr, R., and Jhoti, H. (2003) Oxidation state of the active-site cysteine in protein tyrosine phosphatase 1B, *Nature* 423, 773-777.
77. Raftery, M. J., Yang, Z., Valenzuela, S. M., and Geczy, C. L. (2001) Novel intra- and inter-molecular sulfinamide bonds in S100A8 produced by hypochlorite oxidation, *J Biol Chem* 276, 33393-33401.
78. Poor, C. B., Chen, P. R., Duguid, E., Rice, P. A., and He, C. (2009) Crystal structures of the reduced, sulfenic acid, and mixed disulfide forms of SarZ, a redox active global regulator in *Staphylococcus aureus*, *J Biol Chem* 284, 23517-23524.
79. Legler, P. M., Kumaran, D., Swaminathan, S., Studier, F. W., and Millard, C. B. (2008) Structural characterization and reversal of the natural organophosphate resistance of a D-type esterase, *Saccharomyces cerevisiae* S-formylglutathione hydrolase, *Biochemistry* 47, 9592-9601.
80. Michalek, R. D., Nelson, K. J., Holbrook, B. C., Yi, J. S., Stridiron, D., Daniel, L. W., Fetrow, J. S., King, S. B., Poole, L. B., and Grayson, J. M. (2007) The requirement of reversible cysteine sulfenic acid formation for T cell activation and function, *J Immunol* 179, 6456-6467.
81. Race, P. R., Bentley, M. L., Melvin, J. A., Crow, A., Hughes, R. K., Smith, W. D., Sessions, R. B., Kehoe, M. A., McCafferty, D. G., and Banfield, M. J. (2009) Crystal structure of *Streptococcus pyogenes* sortase A: implications for sortase mechanism, *J Biol Chem* 284, 6924-6933.

82. Willett, W. S., and Copley, S. D. (1996) Identification and localization of a stable sulfenic acid in peroxide-treated tetrachlorohydroquinone dehalogenase using electrospray mass spectrometry, *Chem Biol* 3, 851-857.
83. Arakawa, T., Kawano, Y., Katayama, Y., Nakayama, H., Dohmae, N., Yohda, M., and Odaka, M. (2009) Structural basis for catalytic activation of thiocyanate hydrolase involving metal-ligated cysteine modification, *J Am Chem Soc* 131, 14838-14843.
84. Arakawa, T., Kawano, Y., Kataoka, S., Katayama, Y., Kamiya, N., Yohda, M., and Odaka, M. (2007) Structure of thiocyanate hydrolase: a new nitrile hydratase family protein with a novel five-coordinate cobalt(III) center, *J Mol Biol* 366, 1497-1509.
85. Baker, L. M., and Poole, L. B. (2003) Catalytic mechanism of thiol peroxidase from *Escherichia coli*. Sulfenic acid formation and overoxidation of essential CYS61, *J Biol Chem* 278, 9203-9211.
86. Xu, Z., Lam, L. S., Lam, L. H., Chau, S. F., Ng, T. B., and Au, S. W. (2008) Molecular basis of the redox regulation of SUMO proteases: a protective mechanism of intermolecular disulfide linkage against irreversible sulfhydryl oxidation, *FASEB J* 22, 127-137.
87. Denu, J. M., and Tanner, K. G. (1998) Specific and reversible inactivation of protein tyrosine phosphatases by hydrogen peroxide: evidence for a sulfenic acid intermediate and implications for redox regulation, *Biochemistry* 37, 5633-5642.
88. Wilson, M. A., Ringe, D., and Petsko, G. A. (2005) The atomic resolution crystal structure of the YajL (ThiJ) protein from *Escherichia coli*: a close prokaryotic homologue of the Parkinsonism-associated protein DJ-1, *J Mol Biol* 353, 678-691.
89. Depuydt, M., Leonard, S. E., Vertommen, D., Denoncin, K., Morsomme, P., Wahni, K., Messens, J., Carroll, K. S., and Collet, J. F. (2009) A periplasmic reducing system protects single cysteine residues from oxidation, *Science* 326, 1109-1111.
90. Gurmu, D., Lu, J., Johnson, K. A., Nordlund, P., Holmgren, A., and Erlandsen, H. (2009) The crystal structure of the protein YhaK from *Escherichia coli* reveals a new subclass of redox sensitive enterobacterial bicupins, *Proteins* 74, 18-31.