

Contents

Preface	v
Contributors	vii
1 Genetics and Genomics of Sulfate Respiration in <i>Desulfovibrio</i>	1
<i>Judy D. Wall, Adam P. Arkin, Nurgul C. Balci, Barbara Rapp-Giles</i>	
1.1 Introduction	1
1.2 Approach	2
1.3 Sulfate Metabolism	5
1.4 Lactate Oxidation	6
1.5 Hydrogenases	7
1.6 Transmembrane Electron-Conducting Complexes	8
1.7 Conclusions	9
References	11
2 Living on Sulfate: Three-Dimensional Structure and Spectroscopy of Adenosine 5'-Phosphosulfate Reductase and Dissimilatory Sulfite Reductase	13
<i>Günter Fritz, Alexander Schiffer, Anke Behrens, Thomas Büchert, Ulrich Ermler, Peter M.H. Kroneck</i>	
2.1 Introduction	13
2.2 Adenosine 5'-Phosphosulfate Reductase	14
2.2.1 Molecular Properties of APSR	15
2.2.2 Three-Dimensional Structure of APSR	17
2.2.3 Reaction Mechanism of APSR	17
2.3 Dissimilatory SIR	20
References	21
3 Respiratory Membrane Complexes of <i>Desulfovibrio</i>	24
<i>Inês A. Cardoso Pereira</i>	
3.1 Introduction	24
3.2 Membrane Complexes Conserved in Sulfate Reducers	25

3.2.1	The Qmo Complex	26
3.2.2	The Dsr Complex	29
3.3	Membrane Complexes Found Only in <i>Desulfovibrio</i> spp.	30
3.3.1	The Hmc and 9Hc Complexes	31
3.3.2	The Tmc Complex	31
3.4	Conclusions.	32
	References	33
4	Biochemical and Evolutionary Aspects of Eukaryotes That Inhabit Sulfidic Environments	36
	<i>Ursula Theissen, William Martin</i>	
4.1	Introduction.	36
4.2	Animals in Sulfidic Environments	37
4.3	Sulfide-Oxidizing Enzymes in Eukaryotes.	38
4.4	The Possible Functions of SQR-Related Genes in Eukaryotes	39
4.5	Sulfide and Eukaryotic Evolution.	40
4.6	Conclusion	42
	References	43
5	Evolution and Ecology of Microbes Dissimilating Sulfur Compounds: Insights from Siroheme Sulfite Reductases	46
	<i>Alexander Loy, Stephan Duller, Michael Wagner</i>	
5.1	Introduction.	46
5.2	Evolution of Dissimilatory Sulfite Reductases.	47
5.2.1	Sulfate/Sulfite-Reducing Microorganisms	47
5.2.2	DsrAB-Containing Syntrophs: Former Sulfate/Sulfite-Reducing Microorganisms?	50
5.2.3	Sulfur-Oxidizing Bacteria.	51
5.2.4	The Root and Major Branches of the DsrAB Tree	52
5.2.5	Other Non-DsrAB Dissimilatory Sulfite Reductases	52
5.3	Molecular Insights into the Ecology of DsrAB-Employing Microorganisms	53
5.3.1	PCR-Based Surveys	53
5.3.2	Metagenomics.	54
5.4	Conclusions.	55
	References	56
6	Genomic and Evolutionary Perspectives on Sulfur Metabolism in Green Sulfur Bacteria	60
	<i>Niels-Ulrik Frigaard, Donald A. Bryant</i>	
6.1	Introduction.	60

6.1.1	Green Sulfur Bacteria	61
6.1.2	Genome Sequencing Projects of Green Sulfur Bacteria	62
6.2	Compounds Oxidized by Green Sulfur Bacteria	63
6.3	Enzymes Involved in Sulfur-Compound Oxidation	65
6.3.1	Overview of the Putative Sulfur Compound Oxidation Enzymes.	66
6.3.2	Dissimilatory Sulfite Reductase	66
6.3.3	Sulfide:Quinone Reductase.	67
6.3.4	Flavocytochrome c	69
6.3.5	Sulfite Oxidation.	69
6.3.6	Thiosulfate Oxidation by the Sox System	70
6.3.7	A Novel Complex: SoyYZ	71
6.4	Assimilatory Sulfur Metabolism.	71
6.5	Possible Phage-Mediated Lateral Gene Transfer	72
6.6	Conclusions.	72
	References	73
7	Differential-Expression Proteomics for the Study of Sulfur Metabolism in the Chemolithoautotrophic <i>Acidithiobacillus ferrooxidans</i>	77
	<i>Lissette Valenzuela, An Chi, Simón Beard, Jeffrey Shabanowitz, Donald F. Hunt, Carlos A. Jerez</i>	
7.1	Introduction.	77
7.2	Sulfur Metabolism in <i>A. ferrooxidans</i>	78
7.3	Proteomics of <i>A. ferrooxidans</i> Grown in Sulfur Compounds	78
7.4	Thiosulfate Sulfur Transferases from <i>A. ferrooxidans</i>	79
7.5	Other Proteins Involved in Sulfur Metabolism.	82
7.6	High-Throughput Proteomics of Periplasmic Proteins Induced by Growth of <i>A. ferrooxidans</i> on Sulfur Compounds.	83
7.7	Conclusions.	85
	References	85
8	Sulfur and Light? History and “Thiology” of the Phototrophic Sulfur Bacteria.	87
	<i>Hans G. Trüper</i>	
8.1	Introduction.	88
8.2	Discovery of Sulfur-Oxidizing Microorganisms	88
8.3	Identification of Conspicuous Inclusions as Sulfur	89
8.4	Enrichment Cultures – First Taxonomy – and the Question of Photosynthesis	91
8.5	Pure Cultures of Phototrophic Sulfur Bacteria at Last!	92

8.6	The Age of Enzymology and Isotope Labeling	93
8.7	Advent of Molecular Genetics	95
8.8	Further Reading	96
	References	97
9	Thiosulfate and Sulfur Oxidation in Purple Sulfur Bacteria	101
	<i>Frauke Grimm, Bettina Franz, Christiane Dahl</i>	
9.1	Introduction.	101
9.2	Oxidation of Thiosulfate in <i>A. vinosum</i>	103
9.2.1	sox Genes in <i>A. vinosum</i>	104
9.2.2	Sox Proteins in <i>A. vinosum</i>	105
9.2.3	Inactivation and Complementation of sox Genes in <i>A. vinosum</i>	106
9.3	Oxidation of Stored Sulfur in <i>A. vinosum</i>	107
9.3.1	The <i>dsr</i> Operon and Proteins Encoded Therein.	107
9.3.2	Distribution of <i>dsr</i> Genes in Organisms with Dissimilatory Sulfur Metabolism and Phylogenetic Analysis	108
9.3.3	Model of the Sulfur Oxidation Pathway in <i>A. vinosum</i>	111
9.4	Conclusions.	113
	References	113
10	Sulfur Oxidation in <i>Chlorobium tepidum</i> (syn. <i>Chlorobaculum tepidum</i>): Genetic and Proteomic Analyses	117
	<i>Leong-Keat Chan, Rachael Morgan-Kiss, Thomas E. Hanson</i>	
10.1	Introduction.	117
10.1.1	Background.	117
10.1.2	Sulfur-Compound Dynamics in <i>C. tepidum</i> Batch Cultures.	118
10.2	Genetic Analyses	120
10.2.1	Organization of Genes Encoding Putative Sulfur Oxidation Functions.	120
10.2.2	Mutations Affecting Sulfur Oxidation Have Secondary Effects on Light Harvesting	120
10.2.3	Additional Genetic Techniques Are Needed	121
10.3	Proteomic Analysis.	122
10.3.1	Why Proteomics?	122
10.3.2	Proteomic Analysis of Subcellular Fractions.	122
10.4	Conclusions.	124
	References	125

11	Structural Insights into Component SoxY of the Thiosulfate-Oxidizing Multienzyme System of <i>Chlorobaculum thiosulfatophilum</i>	127
	<i>Jan Stout, Lina De Smet, Bjorn Vergauwen, Savvas Savvides, Jozef Van Beeumen</i>	
11.1	Introduction	127
11.2	SoxY Structure	128
11.2.1	Overall Structure	128
11.2.2	SoxY Monomer	130
11.2.3	SoxY Dimer	130
11.2.4	SoxY Tetramer	131
11.2.5	Location of the Disulfide Bridges and the Potential Sulfur Binding Site	132
11.3	Discussion	133
	References	136
12	Redox Control of Chemotrophic Sulfur Oxidation of <i>Paracoccus pantotrophus</i>	139
	<i>Cornelius G. Friedrich, Armin Quentmeier, Frank Bardischewsky, Dagmar Rother, Grazyna Orawski, Petra Hellwig, Jörg Fischer</i>	
12.1	The Sulfur-Oxidizing Enzyme System of <i>Paracoccus pantotrophus</i>	139
12.2	Abundance of the <i>sox</i> Genes in Bacteria	142
12.3	The Physiological Function of the Flavoprotein SoxF	144
12.4	The Periplasmic Partners of SoxV for Transfer of Electrons	146
	References	148
13	Bacterial Sulfite-Oxidizing Enzymes – Enzymes for Chemolithotrophs Only?	151
	<i>Ulrike Kappler</i>	
13.1	Introduction – Sulfite in the Environment and in Cell Metabolism	151
13.2	Sulfite-Oxidizing Enzymes	152
13.3	Structure and Function of Sulfite-Oxidizing Enzymes	153
13.4	Phylogeny of Sulfite-Oxidizing Enzymes	154
13.5	Diversity of Enzymes Within the Sulfite Oxidase Family	157
13.5.1	Group 1 – SOE Like Enzymes Originating from Pathogenic Microorganisms	157
13.5.1.1	Group 1A Enzymes: YedY and Related Proteins	158
13.5.1.2	Group 1B – 30-kDa Mo-Domain Proteins	159

13.5.2	Group 2: “Classic” Sulfite-Oxidizing Enzymes and Nitrate Reductases	161
13.5.2.1	Group 2A: Sulfite Oxidases and Plant Nitrate Reductases	161
13.5.2.2	Group 2B: SoxCD-Like Enzymes – “Sulfur Dehydrogenases”	162
13.5.2.3	Group 2C: SorAB-Like Sulfite Dehydrogenases	163
13.5.2.4	Other Sulfite-Oxidizing Enzymes in Group 2	164
13.5.3	Group 3: Sulfite-Oxidizing Enzymes – Enzymes from Archaea, Phototrophic and Soil Bacteria.	164
13.6	Conclusions.	165
	References	166
14	Sulfonates and Organotrophic Sulfite Metabolism	170
	<i>Alasdair M. Cook, Theo H.M. Smits, Karin Denger</i>	
14.1	Introduction.	170
14.2	Biosynthesis of Organosulfonates	173
14.3	Dissimilation of Organosulfonates	175
14.4	The Detoxification or Fate of Sulfite	176
14.5	Sulfite Dehydrogenases in Sulfonate Metabolism	178
14.6	Conclusions.	180
	References	181
15	Oxidation of Sulfur and Inorganic Sulfur Compounds in <i>Acidianus ambivalens</i>.	184
	<i>Arnulf Kletzin</i>	
15.1	Introduction.	184
15.2	Sulfur and Sulfur Oxidation	186
15.3	<i>A. ambivalens</i> and <i>A. tengchongensis</i> SORs	188
15.3.1	SOR 3D Structure	190
15.3.2	SOR Subunit and Active-Site Structure	194
15.3.3	SOR Reaction Mechanism	194
15.4	Oxidation of Soluble Sulfur Compounds in <i>Acidianus</i>	196
15.4.1	Sulfite:Acceptor Oxidoreductase	196
15.4.2	Thiosulfate:Quinone Oxidoreductase	197
15.4.3	Tetrathionate Hydrolase	197
15.4.4	Sulfide:Quinone Oxidoreductase	198
15.5	Conclusions.	198
	References	199

16	A Novel Coenzyme F₄₂₀ Dependent Sulfite Reductase and a Small Sulfite Reductase in Methanogenic Archaea	202
	<i>Eric F. Johnson, Biswarup Mukhopadhyay</i>	
16.1	Introduction	202
16.2	Incompatibility of Methanogenesis and Sulfate Reduction, Sulfite As the Key Determinant	206
16.3	Inevitable Exposure of a Methanogen to Sulfite in Hydrothermal Vents and on Early Earth.	206
16.4	Use of Sulfite As a Sulfur Source by <i>Methanocaldococcus jannaschii</i> and Other Methanogens	207
16.5	Expression of a Novel Coenzyme F ₄₂₀ Dependent Sulfite Reductase in <i>Methanocaldococcus jannaschii</i> During Growth on Sulfite	207
16.6	Fsr, Combining Structural Components of Two Different Dissimilatory Metabolic Machineries to Bring About a Sulfite Reduction Function	209
16.7	Purified Fsr Exhibits Properties Predicted from the Primary Structure	210
16.8	Fsr, a Sulfite Detoxification Tool and an Assimilatory Enzyme.	211
16.9	Homologs of Fsr in Other Organisms.	212
16.10	Small Sulfite Reductases in Methanogens	212
16.11	Conclusion and Hypotheses	213
	References	214
17	Archaeal and Bacterial Sulfur Oxygenase-Reductases: Genetic Diversity and Physiological Function	217
	<i>Shuang-Jiang Liu</i>	
17.1	Introduction.	217
17.2	Diversity of Archaeal SORs	219
17.2.1	SOR _{Ab} from <i>A. brierleyi</i>	219
17.2.2	SOR _{Aa} from <i>A. ambivalens</i>	220
17.2.3	SOR _{At} from <i>A. tengchongensis</i>	220
17.2.4	SOR _{St} from <i>S. tokodaii</i>	220
17.2.5	SOR _{Sm} from <i>S. metallicus</i>	221
17.3	Efforts To Identify Bacterial SORs.	221
17.3.1	SOR _{Aqa} from <i>A. aeolicus</i>	221
17.3.2	SOR _{Act} from <i>Acidithiobacillus</i> sp. strain SM-1	221
17.4	SOR Links Elemental Sulfur Oxidation to ATP Synthesis via Sulfite:Acceptor Oxidoreductase and Thiosulfate:Acceptor Oxidoreductase	222
17.5	Physiological Regulation of SOR Activity in Archaea	223
	References	223

18 Diversity of Halophilic Sulfur-Oxidizing Bacteria in Hypersaline Habitats.	225
<i>Dimitry Y. Sorokin</i>	
18.1 Introduction.	225
18.2 Description of Habitats Investigated.	226
18.3 Enrichment Strategy	227
18.4 Moderately Halophilic Aerobic SOB.	228
18.5 Extremely Halophilic Aerobic SOB.	232
18.6 Moderately Halophilic Thiodenitrifiers.	232
18.7 Extremely Halophilic Denitrifying SOB	233
18.8 Oxidation of Thiocyanate at High Salt.	234
18.9 Fatty Acids in the Membrane Lipids	234
18.10 Conclusions and Future Perspectives	235
References	236
19 Sulfur Oxidation at Deep-Sea Hydrothermal Vents.	238
<i>Stefan M. Sievert, Michael Hügler, Craig D. Taylor, Carl O. Wirsen</i>	
19.1 Introduction.	238
19.2 Types of Sulfur-Oxidizing Bacteria	239
19.2.1 Symbiotic Sulfur-Oxidizing Bacteria.	239
19.2.2 Free-Living Sulfur-Oxidizing Bacteria.	241
19.2.2.1 <i>Gammaproteobacteria</i>	241
19.2.2.2 <i>Epsilonproteobacteria</i>	241
19.2.2.3 <i>Aquificaceae</i>	246
19.2.2.4 Carbon Metabolism in Sulfur-Oxidizing Bacteria	246
19.3 Sulfur Oxidation Pathways	247
19.3.1 Types of Pathways	247
19.3.2 Endosymbionts	248
19.3.3 Free-Living Sulfur-Oxidizing Bacteria.	248
19.3.3.1 <i>Beggiatoa</i>	248
19.3.3.2 <i>Thiomicrospira crunogena</i> and <i>Epsilonproteobacteria</i>	249
19.3.3.3 Oxidation of H ₂ by Sulfur-Oxidizing Bacteria	250
19.4 “Snowblower” Vents As Signs for Sulfide Oxidation in the Subseafloor	251
19.4.1 The Subseafloor Biosphere.	251
19.4.2 Filamentous-Sulfur Formation in the Laboratory.	251
19.4.3 “Snowblowers”	252
19.4.4 Diversity of Filamentous-Sulfur-Forming Bacteria	252
19.5 Conclusions and Outlook	253
References	254

20 Speciation Analysis of Microbiologically Produced Sulfur by X-ray Absorption Near Edge Structure Spectroscopy . . .	259
<i>Alexander Prange</i>	
20.1 Introduction	259
20.2 XAS: X-ray Absorption Near-Edge Structure and Extended X-ray Absorption Fine Structure	260
20.2.1 Experimental	260
20.2.2 Advantages of XANES Spectroscopy	264
20.2.3 Sample Preparation	264
20.2.4 Quantitative Analysis of XANES Spectra	265
20.3 Sulfur K-Edge XANES Spectroscopy and Speciation of Microbiologically Produced Sulfur	266
20.3.1 Speciation of Sulfur in Sulfur Globules of Phototrophic and Chemotrophic Sulfur Bacteria	267
20.3.2 Speciation of “Elemental Sulfur” Taken Up by <i>A. vinosum</i>	269
References	270
21 Controls on Isotope Fractionation During Dissimilatory Sulfate Reduction	273
<i>Joost Hoek, Donald E. Canfield</i>	
21.1 Introduction	273
21.2 Sulfur Isotope Fractionation During Dissimilatory Sulfate Reduction	275
21.2.1 Pure Cultures	275
21.2.2 Natural Populations	276
21.3 Stepwise Reduction of Sulfate and Sulfur Isotope Fractionation Models	277
21.4 Multiple Sulfur Isotopes	279
21.5 Conclusions and Future Research	282
References	283
22 Bioprocess Engineering of Sulfate Reduction for Environmental Technology	285
<i>Piet N.L. Lens, Roel J.W. Meulepas, Ricardo Sampaio, Marcus Vallero, Giovanni Esposito</i>	
22.1 Introduction	285
22.2 Sulfate Reduction in Methanogenic Wastewater Treatment	286
22.3 Sulfate-Reducing Bioreactors	288
22.3.1 High-Rate Sulfate-Reducing Bioreactors	288
22.3.1.1 Inocula	288
22.3.1.2 Electron Donor	289
22.3.2 Passive Sulfate-Reducing Systems	291

22.4	Sulfate Reduction for Metal Recovery/Reuse	292
22.4.1	Metal Sulfide Precipitation	292
22.4.2	Biogenic Sulfide for Metal Sulfide Precipitation	292
22.4.3	Selective Metal Precipitation	293
	References	293
23	Impact of Nitrate on the Sulfur Cycle in Oil Fields	296
	<i>Gerrit Voordouw</i>	
23.1	Introduction	296
23.2	The Oil Field Sulfur Cycle	297
23.3	Effect of Nitrate Injection on SRB Physiology	298
23.4	Mechanism of Souring Control	300
23.5	Prospects for Nitrate Injection	301
	References	301
	Index	303