

# *Arsenic*

## *Environmental Geochemistry, Mineralogy, and Microbiology*

79      *Reviews in Mineralogy and Geochemistry*      79

### **TABLE OF CONTENTS**

#### **1      The Environmental Geochemistry of Arsenic: An Overview**

*Robert J. Bowell, Charles N. Alpers, Heather E. Jamieson,  
D. Kirk Nordstrom, Juraj Majzlan*

INTRODUCTION .....	1
ARSENIC TOXICITY IN DRINKING WATER.....	2
ARSENIC MINERALOGY AND PRIMARY OCCURRENCE .....	2
ARSENIC IN THE WEATHERING ENVIRONMENT .....	4
Arsenic in secondary minerals and soils .....	4
Arsenic in water.....	4
ANTHROPOGENIC ARSENIC CONTAMINATION.....	7
ARSENIC IN THE BIOSPHERE.....	8
BIOGEOCHEMICAL CYCLING OF ARSENIC.....	9
SUMMARY .....	11
ACKNOWLEDGMENTS.....	12
REFERENCES .....	13

#### **2      Parageneses and Crystal Chemistry of Arsenic Minerals**

*Juraj Majzlan, Petr Drahota,  
Michal Filippi*

INTRODUCTION .....	17
PARAGENESES OF MINERALS OF ARSENIC .....	18
Definitions .....	19
Magmatic-hydrothermal arsenic minerals.....	20
Metamorphic-hydrothermal arsenic minerals.....	22
Arsenic minerals in hot springs and fumarolic gases .....	26
Arsenic minerals in coal .....	26
Arsenic minerals as products of coal combustion .....	28
Arsenic minerals in soil and fluvial systems .....	30
Arsenic minerals in mine wastes .....	44
Arsenic minerals in underground spaces .....	70

CRYSTAL CHEMISTRY OF ARSENIC MINERALS.....	78
Hierarchical organization of crystal structures.....	79
Crystal chemistry of arsenates.....	79
Crystal chemistry of arsenites and arsenites-arsenates.....	131
Uranyl arsenates and arsenate-arsenites.....	144
Arsenates and arsenites with unknown structure.....	144
Arsenides, sulfarsenides, and sulfides with arsenic, including sulfosalts.....	147
ACKNOWLEDGMENTS.....	148
REFERENCES.....	150
APPENDIX 1: Index of arsenic minerals.....	174
APPENDIX 2: Index of arsenic-bearing minerals.....	184

### **3 Arsenic Speciation and Sorption in Natural Environments**

*Kate M. Campbell, D. Kirk Nordstrom*

INTRODUCTION.....	185
AQUEOUS INORGANIC ARSENIC SPECIES.....	186
Complexation.....	186
Polymerization.....	189
ORGANIC ARSENIC COMPOUNDS AND INTERACTIONS WITH ORGANIC MATTER.....	189
Organic arsenical compounds.....	189
Arsenic complexation and reaction with natural organic matter.....	190
SURFACE COMPLEXATION AND COMPETITIVE SORPTION.....	195
Characterization and chemistry of arsenic surface species.....	197
Effect of competitively adsorbing ions.....	198
Effect of mineral transformations on arsenic speciation and vice-versa.....	200
ARSENIC OXIDATION-REDUCTION REACTIONS AND SPECIATION EFFECTS.....	201
Biogenic redox reactions of arsenic.....	201
Abiotic redox reactions of arsenic.....	201
ARSENIC SPECIATION CALCULATIONS FOR SEVERAL NATURAL WATER COMPOSITIONS.....	204
ACKNOWLEDGMENTS.....	205
REFERENCES.....	210

# 4

## Thermodynamic Properties for Arsenic Minerals and Aqueous Species

*D. Kirk Nordstrom, Juraj Majzlan,  
Erich Königsberger*

INTRODUCTION .....	217
METHODOLOGICAL APPROACH TO INTERNALLY CONSISTENT DATA .....	218
FINDING AN ANCHOR FOR STANDARD STATE PROPERTIES AT 298.15 K, 1 BAR.....	219
Standard state thermodynamic properties of arsenolite, As <sub>2</sub> O <sub>3</sub> (cubic) .....	219
Arsenolite solubility .....	220
Aqueous arsenite and arsenate species.....	221
Standard state thermodynamic properties of claudetite, As <sub>2</sub> O <sub>3</sub> (monoclinic) .....	223
Hydrolysis constants for arsenous and arsenic acids.....	224
SOLUBILITY EQUILIBRIA IN THE Fe(III)-As(V)-H <sub>2</sub> O SYSTEM.....	228
Results and discussion.....	230
A note on solubility constants .....	231
AQUEOUS METAL ARSENATE COMPLEXES .....	233
SUMMARY OF THERMODYNAMIC DATA FOR ARSENATE MINERALS AND RELATED PHASES .....	233
Ca arsenates .....	237
Ba arsenates .....	239
Cu arsenates.....	239
Fe arsenates .....	239
Mg arsenates.....	239
Pb arsenates .....	240
Zn arsenates.....	240
Arsenates with multiple cations.....	240
ARSENIDES AND SULFIDES .....	245
GASEOUS SPECIES.....	245
CONCLUDING REMARKS.....	245
ACKNOWLEDGMENTS.....	249
REFERENCES .....	249

**Color Plates**

CP1-CP16

<b>5</b>	<b>Arsenic Speciation in Solids Using X-ray Absorption Spectroscopy</b>	
	<i>Andrea L. Foster, Christopher S. Kim</i>	
INTRODUCTION .....		257
X-ray absorption spectroscopy (XAS): the “gold standard” for determination of arsenic species in solid phases.....		258
PREPARING, COLLECTING, AND PROCESSING BULK XAS DATA AND M-XAS, XRF, AND XRD DATA.....		261
Characterizing samples prior to beamtime .....		261
Preparing samples for bulk As-XAS data collection .....		263
Collecting XAS spectra, $\mu$ -XRF maps, and $\mu$ -XRD patterns.....		265
Processing XAS spectra .....		268
Processing $\mu$ -XRF maps and $\mu$ -XRD patterns .....		270
XAS DATA ANALYSIS .....		271
Identifying As oxidation states .....		271
Determining the relative abundance of As oxidation states or As species .....		273
Mapping arsenic oxidation states using $\mu$ XRF.....		275
Characterizing the structure of solid-phase arsenic species at the molecular-scale ..		276
Analyzing bulk and microbeam datasets using multivariate techniques .....		279
XAS STUDIES OF ARSENIC SPECIATION IN SOLIDS .....		280
Arsenic mineralogy .....		280
Arsenic oxyanion sorption on mineral surfaces and soils .....		284
Effects of microbial activity on sorbed arsenic species.....		293
XAS studies of rocks and related soils.....		295
Arsenic species in ore, mine wastes, and mining-impacted soil .....		300
Arsenic species in floodplain, aquatic, and organic-rich sediments.....		304
Arsenic species in aquifer sediments.....		306
Arsenic species in wastes from industry, agriculture, and the built environment .....		308
Arsenic species in bioaccessibility and bioavailability test materials .....		316
Arsenic species in biota .....		318
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH		
DIRECTIONS IN As XAS SPECTROSCOPY .....		326
Model systems.....		326
Environmental samples.....		327
General recommendations.....		328
REFERENCES .....		329
APPENDIX 1: XAS studies of As sorption in model systems .....		346
APPENDIX 2: XAS studies of naturally-occurring As-bearing biogenic minerals and laboratory studies of microbial oxidation/reduction of As-bearing biogenic minerals or synthetic analogs.....		351
APPENDIX 3: XAS studies of arsenic speciation in rocks, related soils, and rock-forming fluids. ....		353
APPENDIX 4: XAS studies of As speciation in ore, mine wastes, and mining-impacted sites. ....		355
APPENDIX 5: Arsenic speciation in floodplain and aquatic sediments, and in organic-rich deposits .....		358

APPENDIX 6: Arsenic speciation in bedrock and sedimentary aquifers .....	361
APPENDIX 7: XAS studies of arsenic-rich agricultural, industrial, and municipal wastes .....	363
APPENDIX 8: As-XAS studies to improve sequential extraction, <i>in vitro</i> bioaccessibility (IVBA), and <i>in vivo</i> relative bioavailability (RBA) tests for arsenic .....	366
APPENDIX 9: XAS studies of arsenic speciation in biota. ....	367

## **6 Measuring Arsenic Speciation in Environmental Media: Sampling, Preservation, and Analysis**

*Matthew I. Leybourne, Karen H. Johannesson  
Alemayehu Asfaw*

INTRODUCTION .....	371
Arsenic species .....	372
FIELD COLLECTION AND ANALYSIS .....	373
Solid samples .....	373
Aqueous samples .....	375
Gaseous samples .....	377
LABORATORY ANALYSIS .....	379
Solid samples .....	379
Aqueous samples .....	380
Gaseous samples .....	384
SUMMARY .....	385
ACKNOWLEDGMENTS .....	385
REFERENCES .....	385

## **7 Microbial Arsenic Metabolism and Reaction Energetics**

*Jan P. Amend, Chad Saltikov  
Guang-Sin Lu, Jaime Hernandez*

INTRODUCTION .....	391
ARSENIC METABOLISMS IN BACTERIA AND ARCHAEA .....	392
GENES THAT ENCODE FOR ARSENIC ENZYMES .....	395
Respiratory arsenate reduction via <i>arr</i> .....	395
Detoxifying arsenate reduction via <i>ars</i> .....	397
Aerobic arsenite oxidation via <i>aito</i> .....	397
Anaerobic arsenite oxidation via <i>arx</i> .....	397
ARSENIC REDOX IN ARCHAEA .....	398
ENERGETICS OF ARSENIC REDOX REACTIONS .....	398
CONCLUDING REMARKS .....	404
REFERENCES .....	404
APPENDIX: Archaeal and bacterial isolates capable of metabolizing arsenic .....	414

**8** **Health Risks Associated with Chronic Exposures to Arsenic in the Environment**

*Valerie L. Mitchell*

INTRODUCTION .....435  
PREVALENCE OF ARSENIC IN THE ENVIRONMENT .....435  
    Water.....435  
    Soils .....436  
    Air.....437  
    Food supply .....437  
ARSENIC TOXICITY .....438  
CHRONIC ARSENIC EXPOSURE AND ASSOCIATED HEALTH  
    EFFECTS BY REGION .....439  
        Taiwan .....439  
        Chile .....440  
        Bangladesh .....442  
        United States of America.....443  
ENVIRONMENTAL REGULATION OF ARSENIC IN THE UNITED  
    STATES OF AMERICA .....444  
SUMMARY .....445  
REFERENCES .....445

**9** **Using *In Vivo* Bioavailability and/or *In Vitro* Gastrointestinal Bioaccessibility Testing to Adjust Human Exposure to Arsenic from Soil Ingestion**

*Nicholas T. Basta, Albert Juhasz*

INTRODUCTION .....451  
METHODS FOR DETERMINING BIOAVAILABILITY OF As  
    FROM SOIL INGESTION: *IN VIVO* MODELS.....453  
        Measurement of As relative bioavailability in contaminated soils.....456  
        Comparison of animal models for the determination of As relative bioavailability .458  
USING *IN VITRO* GASTROINTESTINAL BIOACCESSIBILITY  
    METHODS TO PREDICT BIOAVAILABILITY .....458  
        Factors influencing As bioaccessibility and relative bioavailability.....461  
        Correlation of As relative bioavailability and As bioaccessibility.....462  
        Validation of As relative bioavailability-bioaccessibility relationships.....466  
APPLYING As RELATIVE BIOAVAILABILITY / BIOACCESSIBILITY  
    TO THE CHARACTERIZATION OF As RISK IN SOILS .....467  
FUTURE DIRECTIONS, KNOWLEDGE GAPS, AND RESEARCH CHALLENGES ....468  
REFERENCES .....469

# 10

## The Characterization of Arsenic in Mine Waste

*Dave Craw, Robert J. Bowell*

INTRODUCTION .....	473
ARSENIC IN DIFFERENT MINERAL DEPOSIT TYPES .....	473
SECONDARY ARSENIC MINERALS IN MINE WASTES .....	474
Arsenic solubility in mine waste .....	478
Environmental issues associated with arsenic in mine wastes .....	479
Bioavailability/bioaccessibility of arsenic in mine waste.....	479
Toxicity of arsenic in mine waste .....	482
GEOLOGICAL CONTROLS ON ARSENIC IN MINE WASTE.....	484
GOLD MINING AND PROCESSING.....	486
CASE STUDIES: NEW ZEALAND GOLD MINES .....	488
Arsenopyrite oxidation in orogenic gold mines .....	490
Iron-poor orogenic gold mine wastes.....	492
Iron-rich orogenic gold mine wastes .....	494
Modern Macraes orogenic gold mine.....	495
Epithermal gold mines.....	498
Epithermal/geothermal spring deposits .....	499
CONCLUSIONS.....	500
REFERENCES .....	501

# 11

## The Management of Arsenic in the Mining Industry

*Robert J. Bowell, Dave Craw*

INTRODUCTION .....	507
APPROACH TO ARSENIC MANAGEMENT .....	509
Waste rock .....	509
Low-grade ore stock piles .....	510
Tailings impoundment.....	510
Contaminated water.....	510
Chemical reagents .....	511
ARSENIC CONTAINMENT .....	511
Physical containment.....	511
Chemical containment.....	515
ARSENIC REMOVAL BY ACTIVE TREATMENT.....	516
Chemical precipitation.....	516
Adsorption .....	518
ARSENIC REMOVAL BY PASSIVE TREATMENT .....	520
Membrane filtration.....	521
<i>In situ</i> treatment.....	523
Biological remediation .....	523
ENVIRONMENTAL ATTENUATION .....	523
Environmental attenuation on minerals.....	524
Phytoextraction.....	524

Phytostabilization .....	524
Phytoisolation .....	525
CONCLUSIONS .....	526
REFERENCES .....	528

## **12                    The Legacy of Arsenic Contamination from Mining and Processing Refractory Gold Ore at Giant Mine, Yellowknife, Northwest Territories, Canada**

*Heather E. Jamieson*

INTRODUCTION .....	533
FACTORS INFLUENCING THE LEGACY OF ARSENIC CONTAMINATION	
AT GIANT MINE .....	537
Nature of mineralization.....	537
Ore roasting .....	539
Waste disposal practices .....	542
REMEDICATION PLAN.....	547
CONCLUSIONS.....	548
REFERENCES .....	549

## **13                    Arsenic Associated with Historical Gold Mining in the Sierra Nevada Foothills: Case Study and Field Trip Guide for Empire Mine State Historic Park, California**

*Charles N. Alpers, Perry A. Myers,  
Daniel Millsap, Tamsen Burlak Regnier*

INTRODUCTION .....	553
GEOLOGICAL SETTING .....	554
Regional geology.....	554
Geology of the Grass Valley area .....	556
MINING HISTORY .....	557
ENVIRONMENTAL STUDIES AT OTHER SIERRA NEVADA GOLD MINES .....	559
Relationship of arsenic to gold mineralization.....	559
Harvard Pit, Jamestown Mining District .....	559
Eagle-Shawmut and Clio Mines, Jacksonville Mining District .....	561
Mesa de Oro and Central Eureka Mine, Amador County .....	562
Argonaut Mine, Amador County .....	563
Lava Cap Mine, Nevada County.....	563
ENVIRONMENTAL CHARACTERIZATION AND REMEDICATION AT EMPIRE MINE STATE HISTORIC PARK .....	564
Osborne Hill Area trails.....	566
Red Dirt Pile.....	566
Characterization of waste-rock piles .....	566



Bioavailability and bioaccessibility of As in soils and waste rock from Empire Mine SHP.....	574
Passive water treatment at Magenta Drain .....	578
FIELD TRIP STOPS.....	580
1. Stamp mill and mine yard .....	580
2. Empire Mine waste dump.....	581
3. Cyanide plant.....	581
4. Prescott shaft and waste pile.....	581
5. Visitor Center.....	581
6. Superintendent's office and other rooms .....	581
7. Magenta Drain constructed wetlands .....	581
CONCLUDING REMARKS.....	583
ACKNOWLEDGMENTS.....	583
REFERENCES .....	583

# 14

## Hydrogeochemistry of the Tsumeb Deposit: Implications for Arsenate Mineral Stability

*Robert J. Bowell*

INTRODUCTION .....	589
LOCATION OF THE TSUMEB MINE .....	589
HISTORY OF THE TSUMEB MINE.....	591
GEOLOGY OF THE TSUMEB DEPOSIT.....	591
HYDROGEOCHEMISTRY OF THE CURRENT MINE.....	595
Shallow stope waters .....	596
Dilute upper stope waters.....	596
Shallow undilute waters.....	600
Intermediate waters .....	603
North Break Fault.....	603
Deep waters .....	603
ARSENIC HYDROGEOCHEMISTRY .....	607
ARSENATE SECONDARY MINERALOGY .....	610
COMPARISON OF MINERALOGY TO HYDROGEOCHEMISTRY .....	613
Copper-zinc arsenate system.....	614
Iron-arsenate system.....	617
Lead-arsenate system.....	617
Zinc-arsenate system .....	620
SUMMARY .....	620
REFERENCES .....	621
APPENDIX 1: Arsenic bearing minerals found at Tsumeb.....	624
APPENDIX 2: Composition of Tsumeb mine waters and classification.....	626
APPENDIX 3: Compilation of Gibbs free energy for secondary arsenate minerals.....	627