REVIEWS IN MINERALOGY AND GEOCHEMISTRY

Volume 79 2014

Arsenic

Environmental Geochemistry, Mineralogy, and Microbiology

EDITORS

Robert J. Bowell

SRK Consulting, Cardiff, United Kingdom

Charles N. Alpers

USGS, California, Ū.S.A.

Heather E. Jamieson

Queen's University, Ontario, Canada

D. Kirk Nordstrom

USGS, Colorado, U.S.A.

Juraj Majzlan

Friedrich-Schiller-Universitat, Jena, Germany

Front Cover: Mimetite, 17-23 Floors, 9th Level, Jersey Vein, Bunker Hill Mine, Kellogg, Idaho, U.S.A. Field of view 3 cm. Crystal drawing of mimetite crystal structure.

Back Cover: (*top left*) Erythrite crystals, Bou Azer District, Tazenakht, Ouarzazate Province, Souss-Massa-Draâ Region, Morocco. Field of view 2 cm. (*top right*) Arthurite, scorodite and pharmacosiderite, 150 level Copper Stope, Majuba Mine, Pershing County, Nevada, U.S.A. Field of view 1.2 cm. (*bottom left*) Shultenite (white) in matrix of Cuprian adamite (emerald green) and olivenite (dark green) nest of crystals in tennantite matrix, Tsumeb Mine, Tsumeb, Otjikoto region, Namibia. Field of view 2.5 cm (*bottom right*) Liroconite, Wheal Gorland, St Day, Cornwall, United Kingdom. Field of view 3 cm.

Series Editor: **Jodi J. Rosso**

MINERALOGICAL SOCIETY of AMERICA GEOCHEMICAL SOCIETY

Arsenic

Environmental Geochemistry, Mineralogy, and Microbiology

79 <i>i</i>	Reviews	in M	'ineral	ogv	and	Geoche	mistrv	79
-------------	---------	------	---------	-----	-----	--------	--------	----

TABLE OF CONTENTS

The Environmental Geochemistry of Arsenic: An Overview

1

Robert J. Bowell, Charles N. Alpers, H D. Kirk Nords	eather E. Jamieson, trom, Juraj Majzlan
INTRODUCTION	
ARSENIC TOXICITY IN DRINKING WATER	
ARSENIC MINERALOGY AND PRIMARY OCCURRENCE	2
ARSENIC IN THE WEATHERING ENVIRONMENT	4
Arsenic in secondary minerals and soils	
Arsenic in water	
ANTHROPOGENIC ARSENIC CONTAMINATION	7
ARSENIC IN THE BIOSPHERE	
BIOGEOCHEMICAL CYCLING OF ARSENIC	9
SUMMARY	
ACKNOWLEDGMENTS	
REFERENCES	
Juraj Ma	jzlan, Petr Drahota, Michal Filippi
INTRODUCTION	17
PARAGENESES OF MINERALS OF ARSENIC	
Definitions	
Magmatic-hydrothermal arsenic minerals	20
Metamorphic-hydrothermal arsenic minerals	
Arsenic minerals in hot springs and fumarolic gases	26
Arsenic minerals in coal	
Arsenic minerals as products of coal combustion	
Arsenic minerals in soil and fluvial systems	
Arsenic minerals in mine wastes	
Arsenic minerals in underground spaces	70
vii	

Arsenic – Table of Contents

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	
Arsenates and arsenites with unknown structure	144
Arsenides, sulfarsenides, and sulfides with arsenic, including sulfosalts	
ACKNOWLEDGMENTS	148
REFERENCES	
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 No	rdstrom
INTRODUCTION	185
AQUEOUS INORGANIC ARSENIC SPECIES	
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	
Effect of mineral transformations on arsenic speciation and vice-versa	200
ARSENIC OXIDATION-REDUCTION REACTIONS	
AND SPECIATION EFFECTS	
Biogenic redox reactions of arsenic	
Abiotic redox reactions of arsenic	201
ARSENIC SPECIATION CALCULATIONS FOR	
SEVERAL NATURAL WATER COMPOSITIONS	
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	217
INTERNALLY CONSISTENT DATA	218
FINDING AN ANCHOR FOR STANDARD STATE	210
	210
PROPERTIES AT 298.15 K, 1 BAR	
Standard state thermodynamic properties of arsenolite, As ₂ O ₃ (cubic)	
Arsenolite solubility	220
Aqueous arsenite and arsenate species	
Standard state thermodynamic properties of claudetite, As ₂ O ₃ (monoclinic)	
Hydrolysis constants for arsenous and arsenic acids	
SOLUBILITY EQUILIBRIA IN THE FE(III)-As(V)-H ₂ O SYSTEM	
Results and discussion	
A note on solubility constants	
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	
Zn arsenates	240
Arsenates with multiple cations	240
ARSENIDES AND SULFIDES	
GASEOUS SPECIES	245
CONCLUDING REMARKS	
ACKNOWLEDGMENTS.	
DEEDENCES	2.40

Color Plates

CP1-CP16

5

Arsenic Speciation in Solids Using X-ray Absorption Spectroscopy

Andrea L. Foster, Christopher S. Kim

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, μ-XRF maps, and μ-XRD patterns	265
Processing XAS spectra	268
Processing μ-XRF maps and μ-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 µXRF	
Characterizing the structure of solid-phase arsenic species at the molecular-scale.	
Analyzing bulk and microbeam datasets using multivariate techniques	
XAS STUDIES OF ARSENIC SPECIATION IN SOLIDS	
Arsenic mineralogy	
Arsenic oxyanion sorption on mineral surfaces and soils	
Effects of microbial activity on sorbed arsenic species	
XAS studies of rocks and related soils	
Arsenic species in ore, mine wastes, and mining-impacted soil	
Arsenic species in floodplain, aquatic, and organic-rich sediments	
Arsenic species in aquifer sediments	
Arsenic species in wastes from industry, agriculture, and the built environment	
Arsenic species in bioaccessibility and bioavailability test materials	
Arsenic species in biota	318
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH	
DIRECTIONS IN As XAS SPECTROSOCPY	
Model systems	
Environmental samples	
General recommendations	
REFERENCES	
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

Arsenic - Table of Contents

APPENDIX 6: Arsenic speciation in bedrock and sedimentary aquifers	361
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.	
·	
Measuring Arsenic Speciation in Environmental Media: Sampling, Preservation, and Analysis	
Matthew I. Leybourne, Karen H. Johann	esson
Alemayehu A	
INTRODUCTION	371
Arsenic species	372
FIELD COLLECTION AND ANALYSIS	373
Solid samples	373
Aqueous samples	
Gaseous samples	
LABORATORY ANALYSIS	
Solid samples	
Aqueous samples	
Gaseous samples	
SUMMARY	
ACKNOWLEDGMENTS	
REFERENCES	385
Microbial Arsenic Metabolism and Reaction Energetics Jan P. Amend, Chad Sa	ltikov
Guang-Sin Lu. Jaime Herne	ındez
INTRODUCTION	
ARSENIC METABOLISMS IN BACTERIA AND ARCHAEA	
GENES THAT ENCODE FOR ARSENIC ENZYMES	
Respiratory arsenate reduction via arr	
Detoxifying arsenate reduction via ars	
Aerobic arsenite oxidation via aio	
Anaerobic arsenite oxidation via arx	
ARSENIC REDOX IN ARCHAEA	
ENERGETICS OF ARSENIC REDOX REACTIONS	
CONCLUDING REMARKS	
REFERENCES	
APPENDIX: Archaeal and bacterial isolates capable of metabolizing arsenic	414

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

2	
	Valerie L. Mitchel
INTRODUCTION	435
PREVALENCE OF ARSENIC IN THE ENVIRONMENT	
Water	
Soils	
Air	
Food supply	
ARSENIC TOXICITY	
CHRONIC ARSENIC EXPOSURE AND ASSOCIATED HEALTH	
EFFECTS BY REGION	439
Taiwan	
Chile	
Bangladesh	
United States of America	
ENVIRONMENTAL REGULATION OF ARSENIC IN THE UNITED	
STATES OF AMERICA	444
SUMMARY	445
REFERENCES	445
9 Using In Vivo Bioavailability and/or In Vitro Gastroin Bioaccessibility Testing to Adjust Human Expos	
to Arsenic from Soil Ingestion	
Nicholas T. Bo	asta, 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	
Comparison of animal models for the determination of As relative l	
USING IN VITRO GASTROINTESTINAL BIOACCESSIBILITY	siouvunuomity , voc
METHODS TO PREDICT BIOAVAILABILITY	458
Factors influencing As bioaccessibility and relative bioavailability	
Correlation of As relative bioavailability and As bioaccessibility	
Validation of As relative bioavailability-bioaccessibility relationshi	462
APPLYING AS RELATIVE BIOAVAILABILITY / BIOACCESSIBILITY	
	ps466
TO THE CHARACTERIZATION OF As RISK IN SOILS	ps466
	ps466 ,467

10 The Characterization of Arsenic in Mine Waste

Dave	Craw.	Robert J	Row	ρl

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
The Management of Arsenic in the Mining Indust Robert J. Bo	ry well, Dave Craw
Robert J. Bo	owell, Dave Craw
Robert J. Bo	owell, Dave Craw
Robert J. Bo INTRODUCTION	507
INTRODUCTION	507
INTRODUCTION	
INTRODUCTION	
Robert J. Bo INTRODUCTION	
Robert J. Bo INTRODUCTION	
INTRODUCTION	
INTRODUCTION APPROACH TO ARSENIC MANAGEMENT Waste rock Low-grade ore stock piles Tailings impoundment Contaminated water Chemical reagents ARSENIC CONTAINMENT Physical containment	
INTRODUCTION APPROACH TO ARSENIC MANAGEMENT Waste rock Low-grade ore stock piles Tailings impoundment Contaminated water Chemical reagents ARSENIC CONTAINMENT Physical containment Chemical containment	507
INTRODUCTION	507
INTRODUCTION	
INTRODUCTION	507
INTRODUCTION	507
INTRODUCTION	507
INTRODUCTION APPROACH TO ARSENIC MANAGEMENT Waste rock Low-grade ore stock piles Tailings impoundment Contaminated water Chemical reagents ARSENIC CONTAINMENT Physical containment Chemical containment ARSENIC REMOVAL BY ACTIVE TREATMENT Chemical precipitation Adsorption ARSENIC REMOVAL BY PASSIVE TREATMENT Membrane filtration	507
INTRODUCTION APPROACH TO ARSENIC MANAGEMENT Waste rock Low-grade ore stock piles Tailings impoundment Contaminated water Chemical reagents ARSENIC CONTAINMENT Physical containment Chemical containment ARSENIC REMOVAL BY ACTIVE TREATMENT Chemical precipitation Adsorption ARSENIC REMOVAL BY PASSIVE TREATMENT Membrane filtration In situ treatment Biological remediation ENVIRONMENTAL ATTENUATION	507
INTRODUCTION APPROACH TO ARSENIC MANAGEMENT Waste rock Low-grade ore stock piles Tailings impoundment Contaminated water Chemical reagents ARSENIC CONTAINMENT Physical containment Chemical containment ARSENIC REMOVAL BY ACTIVE TREATMENT Chemical precipitation Adsorption ARSENIC REMOVAL BY PASSIVE TREATMENT Membrane filtration In situ treatment Biological remediation	507

Arsenic – Table of Contents

Phytostabilization	524
Phytoisolation	
CONCLUSIONS	
REFERENCES	
The Legacy of Arsenic Contamination from Mining and Processing Refractory Gold Ore at Giant Mine, Yellowknife, Northwest Territories, Canada Heather E. J.	amieson
INTRODUCTION	533
FACTORS INFLUENCING THE LEGACY OF ARSENIC CONTAMINATION	
AT GIANT MINE	537
Nature of mineralization	
Ore roasting	
Waste disposal practices	542
REMEDIATION PLAN	
CONCLUSIONS	
REFERENCES	549
in the Sierra Nevada Foothills: Case Study and Field Trip Guid for Empire Mine State Historic Park, California Charles N. Alpers, Perry A Daniel Millsap, Tamsen Burlak	. Myers,
	Ü
INTRODUCTION	
GEOLOGICAL SETTING	
Regional geology	
Geology of the Grass Valley area	
MINING HISTORY	
ENVIRONMENTAL STUDIES AT OTHER SIERRA NEVADA GOLD MINES	
Relationship of arsenic to gold mineralization	
Harvard Pit, Jamestown Mining District	
Eagle-Shawmut and Clio Mines, Jacksonville Mining District	
Mesa de Oro and Central Eureka Mine, Amador County	
Argonaut Mine, Amador County	
Lava Cap Mine, Nevada County	563
ENVIRONMENTAL CHARACTERIZATION AND	
REMEDIATION AT EMPIRE MINE STATE HISTORIC PARK	
Osborne Hill Area trails	
	566
Red Dirt Pile Characterization of waste-rock piles	566 566

Arsenic - Table of Contents

Bioavailability and bioaccessibilty of As in soils and waste rock	
from Empire Mine SHP	574
Passive water treatment at Magenta Drain	578
FIELD TRIP STOPS	
1. Stamp mill and mine yard	580
2. Empire Mine waste dump	581
3. Cyanide plant	581
4. Prescott shaft and waste pile	
5. Visitor Center	
6. Superintendent's office and other rooms	581
7. Magenta Drain constructed wetlands	581
CONCLUDING REMARKS	583
ACKNOWLEDGMENTS	
REFERENCES	583
Implications for Arsenate Mineral Stability	Robert J. Bowell
INTRODUCTION	589
LOCATION OF THE TSUMEB MINE	
HISTORY OF THE TSUMEB MINE	591
GEOLOGY OF THE TSUMEB DEPOSIT	591
HYDROGEOCHEMISTRY OF THE CURRENT MINE	
Shallow stope waters	596
Dilute upper stope waters	596
Shallow undilute waters	
Intermediate waters	
North Break Fault Deep waters	603
ARSENIC HYDROGEOCHEMISTRY	607
ARSENATE SECONDARY MINERALOGY	610
COMPARISON OF MINERALOGY TO HYDROGEOCHEMISTRY	
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	
AFFEINDIA 2. Composition of Tsumed inflic waters and classification	626