

1**Radioactivity and the 20th Century****Rodney C. Ewing**

INTRODUCTION	1
THE BEGINNING OF THE "ATOMIC ERA": HISTORICAL NOTES	3
Henri Becquerel and the discovery of radioactivity	4
Marie and Pierre Curie	5
Ernest Rutherford and Frederick Soddy	6
Bertram Borden Boltwood	8
THE END OF THE CENTURY:	
THE NUCLEAR FUEL CYCLE INTERSECTS GEOCHEMICAL CYCLES	10
Geochemical cycles of radionuclides	11
Radiation exposure	14
SUMMARY	18
ACKNOWLEDGMENTS	19
REFERENCES	19

2**The Crystal Chemistry of Uranium****Peter C. Burns**

INTRODUCTION	23
STRUCTURES OF U^{4+} MINERALS	24
BONDING IN U^{6+} POLYHEDRA	26
GEOMETRIES OF U^{6+} POLYHEDRA	27
Molecular-orbital calculations	27
EXAFS data	27
X-ray-diffraction data	28
Bond-valence parameters for U^{6+}	29
CONSTRAINTS ON POLYMERIZATION OF URANYL POLYHEDRA	30
HIERARCHY OF URANYL MINERAL STRUCTURES	32
The role of $(OH)^-$ and H_2O in uranyl mineral structures	33
Structures containing sheets of polyhedra	33
Anion topologies with squares	36
Anion topologies with triangles and pentagons	41
Anion topologies with triangles, squares and pentagons	49
Structures containing infinite chains	78
Structures containing finite clusters	82
Structures consisting of frameworks	85
ACKNOWLEDGMENTS	86
REFERENCES	86

3 Systematics and Paragenesis of Uranium Minerals

Robert Finch & Takashi Murakami

INTRODUCTION	91
URANIUM MINERALS SYSTEMATICS	92
Minerals containing reduced uranium	92
Uranium(IV) silicates	97
Uranium(IV) niobates, tantalates and titanates	98
Uranium(IV) phosphates: rhabdophane group	105
Other uranium(IV) minerals	106
Uranyl minerals	107
Uranyl oxyhydroxides	108
Pb-uranyl oxyhydroxides	113
Uranyl carbonates	115
Uranyl silicates	120
Uranyl phosphates and arsenates	124
Uranyl vanadates, molybdates, tungstates	132
Uranyl sulfates, selenites, tellurites	134
ALTERATION OF REDUCED URANIUM MINERALS	137
Uraninite alteration under reducing conditions	138
Uraninite alteration under oxidizing conditions	140
Replacement of uraninite by uranyl minerals	144
ALTERATION OF URANYL MINERALS	146
Thermodynamic background	146
Measured and estimated thermodynamic parameters	146
Dehydration and the role of H ₂ O	152
Groundwater alteration	154
THE ROLE OF RADIOGENIC Pb IN U-MINERAL PARAGENESIS	156
PARAGENESIS OF THE URANYL PHOSPHATES	162
ACKNOWLEDGMENTS	166
REFERENCES	166

4 Stable Isotope Geochemistry of Uranium Deposits

Mostafa Fayek & T. Kurtis Kyser

INTRODUCTION	181
ISOTOPE FRACTIONATION: PRINCIPLES AND PROCESSES	181
Isotope exchange	182
Fractionation factors	183
Isotopic composition of systems and isotopic equilibrium	183
Causes of isotopic variation	184
Stable isotope geothermometry	185
ISOTOPIC COMPOSITION OF HYDROTHERMAL SYSTEMS	186
Open vs. closed system	187
Oxygen and hydrogen isotopes	188
Carbon isotopes	189
Sulfur isotopes	190

Table of Contents

STABLE ISOTOPIC COMPOSITION OF PRINCIPAL FLUID RESERVOIRS.....	192
Seawater	193
Meteoric water.....	193
Magmatic fluids and juvenile waters.....	195
Metamorphic fluids	196
Connate and formation waters, and basinal brines.....	196
STABLE ISOTOPIC STUDIES OF URANIUM DEPOSITS.....	197
Unconformity-type uranium deposits	197
Quartz-pebble conglomerate deposits.....	204
Sandstone-type deposits	208
Vein-type uranium deposits.....	213
CONCLUSIONS.....	214
ACKNOWLEDGMENTS.....	214
REFERENCES.....	214

5 Environmental Aqueous Geochemistry of Actinides

William M. Murphy & Everett L. Shock

INTRODUCTION	221
GENERALITIES OF ENVIRONMENTAL AQUEOUS	
ACTINIDE GEOCHEMISTRY	222
Complications in environmental aqueous actinide geochemistry	223
Aqueous actinides in environmental and geochemical systems.....	225
Uranium and other actinides in hot water.....	226
The effects of pH and oxidation state on the speciation of aqueous U.....	226
CALCULATION OF STANDARD STATE PROPERTIES FOR AQUEOUS	
SPECIES AS FUNCTIONS OF TEMPERATURE AND PRESSURE	231
Estimating the temperature dependence for	
equilibrium association constants	232
Estimating values of $\log \beta$ at 25°C and 1 bar	236
Inorganic complexes	236
Organic complexes	238
Activity coefficients for aqueous actinide ions and complexes.....	243
EXAMPLES OF SPECIATION CALCULATIONS FOR Am(III)	
IN GEOLOGICAL AND ENVIRONMENTAL FLUIDS.....	243
FUTURE DIRECTIONS FOR RESEARCH.....	246
ACKNOWLEDGMENTS.....	246
APPENDIX.....	247
REFERENCES.....	248

6 Uranium Ore Deposits—Products of the Radioactive Earth

Jane A. Plant, Peter R. Simpson, Barry Smith, Brian F. Windley

INTRODUCTION	255
SOME CHARACTERISTICS OF URANIUM	
RADIOACTIVITY AND EARTH PROCESSES	256
SEPARATION OF RADIOTHERMAL CONTINENTAL CRUST	262

Table of Contents

PRIMARY ENRICHMENT OF URANIUM IN FELSIC IGNEOUS ROCKS	264
Tonalite-trondhjemite granitoids	264
"I-type" calc-alkaline orogenic granitoids	264
Late and post-orogenic evolved I-type and A-type granites	266
CRUSTAL EVOLUTION	267
DISTRIBUTION OF RADIOACTIVITY IN THE CONTINENTAL CRUST	270
CLASSIFICATIONS OF URANIUM DEPOSITS	273
URANIUM DEPOSITS OF IGNEOUS PLUTONIC AND VOLCANIC ASSOCIATIONS	274
Changes associated with water-rock interaction in granites	276
Magmatic uranium deposits	280
Metasomatite uranium deposits	283
Breccia-complex uranium deposits	284
Volcanic uranium deposits	286
METAMORPHIC URANIUM DEPOSITS	290
Synmetamorphic uranium deposits	290
Uranium vein deposits in metamorphic rocks	291
URANIUM DEPOSITS OF SEDIMENT AND SEDIMENTARY BASIN ASSOCIATION	292
Quartz-pebble conglomerate uranium deposits	293
Unconformity-related uranium deposits	296
Sandstone uranium deposits	300
Sediment-hosted vein-type uranium deposits	302
Collapse-breccia pipe uranium deposits	303
Lignite uranium deposits	303
Surficial uranium deposits	304
Phosphorite uranium deposits	305
Uraniferous black shale	305
CONCLUSIONS	305
ACKNOWLEDGMENTS	307
REFERENCES	307

7

Mineralogy and Geochemistry of Natural Fission Reactors in Gabon

Janusz Janeczek

INTRODUCTION: NATURAL FISSION REACTORS	321
Geological setting	323
The origin of U deposits in the Franceville basin	324
Reactor zones	325
Physics of natural fission reactors	329
MINERALOGY OF NATURAL FISSION REACTORS	333
Uranium minerals	333
Uraninite	333
Coffinite	343
Uranyl minerals	345
Major associated minerals	347
Clay minerals	347
Galena	349

Table of Contents

Accessory minerals.....	350
Native elements.....	350
Ru-, Rh-, and Pd-bearing minerals	350
Pyrite and other sulfides.....	352
Oxides	353
Calcite.....	354
Phosphates	355
Crandallite group	355
Zircon.....	356
Anomalous isotopic compositions of minerals in the reactor zones	357
URANIFEROUS ORGANIC MATTER.....	361
GEOCHEMISTRY OF NATURAL FISSION REACTORS	365
Actinides, fissiogenic and non-fissiogenic elements	365
Actinides.....	368
Uranium	368
Thorium	372
Plutonium	372
Neptunium	373
Actinide daughters: Bi and Pb	374
Fission products.....	375
Alkali and alkaline earth elements (Rb, Sr, Cs, and Ba).....	375
Rare Earth Elements.....	376
Technetium.....	378
Platinum group elements (PGE): Ru, Rh and Pd.....	379
Low-yield mass region for fission products: Ag, Cd and Te	380
Molybdenum.....	380
Conditions for migration and retention of radionuclides	
in natural fission reactors	381
CONCLUDING REMARKS	385
ACKNOWLEDGMENTS.....	387
REFERENCES.....	387

8

Geomicrobiology of Uranium

Yohey Suzuki & Jillian F. Banfield

INTRODUCTION.....	393
BIOLOGICAL CLASSIFICATION OF METAL IONS	394
THE MICROBIAL CELL—SITES FOR METAL BINDING.....	394
The cytoplasm and cytoplasmic membrane	395
Cell walls and associated surfaces	396
Extracellular polymers	398
MICROBIAL URANIUM ACCUMULATION.....	399
Metabolism-dependent metal uptake	399
Metabolism-independent uptake of uranium.....	401
Models for uranium biosorption	412
URANIUM TOXICITY, TOLERANCE, AND BIOAVAILABILITY.....	414
Toxicity mechanisms in microorganisms.....	415
Factors affecting bioavailability and toxicity of uranium to microorganisms.....	415

Table of Contents

Resistance and tolerance to uranium toxicity	415
MICROBIAL ECOLOGY IN CONTAMINATED SITES	417
Microbial ecology in surficial uranium-contaminated sites and groundwaters	418
IMPLICATIONS FOR UNDERSTANDING GEOLOGICAL PROCESSES	419
Microbial roles in the formation of uranium ore deposits	419
Fossilization of microbial cells	420
Subsurface transport of uranium	421
Microbial impacts on the surface uranium cycle	421
BIOREMEDIATION OF URANIUM—	
AND OTHER ACTINIDES—CONTAMINATED SITES	422
IMPLICATIONS FOR MIGRATION OF OTHER ACTINIDES	422
SUGGESTIONS FOR FUTURE WORK	422
ACKNOWLEDGMENTS	424
REFERENCES	424

9

Uranium Contamination in the Subsurface: Characterization and Remediation

Abdesselam Abdelouas, Werner Lutze, H. Eric Nuttall

INTRODUCTION	433
LEACHING OF CONTAMINANTS FROM U MILL TAILINGS	435
ENVIRONMENTAL IMPACT AND HEALTH RISKS	
OF U MILL TAILINGS	438
Remediation work in the western United States: The UMTRA program	438
Remediation work in Germany by WISMUT	440
Mill tailings in Canada: A case study	441
TECHNIQUES FOR U REMEDIATION	445
Innovative or emerging processes	445
Conventional technologies: Pump-and-treat	447
MICROBIAL REDUCTION OF URANIUM	449
Reduction of uranium	449
Reduction of uranium by microorganisms	450
A laboratory study on bioremediation of uranium in groundwater from a mill tailings site	454
Results	459
SUMMARY AND CONCLUSIONS	467
ACKNOWLEDGMENTS	468
REFERENCES	468

10

Uranium Mineralogy and the Geologic Disposal of Spent Nuclear Fuel

David J. Wronkiewicz & Edgar C. Buck

INTRODUCTION	475
THE STRUCTURE AND COMPOSITION OF SPENT NUCLEAR FUEL	476
THE REPOSITORY ENVIRONMENT	478

Table of Contents

An unsaturated setting	478
Effects of radiation on the repository environment	479
OXIDATION AND DISSOLUTION PROCESSES FOR URANIUM SOLIDS	480
EFFECTS OF SECONDARY URANIUM MINERALS	484
Influence on the dissolution of uranium solids	484
Comparison of corrosion products between spent fuel and UO_2	485
Comparisons with natural analogues	488
Influence of alteration phases on the migration of radionuclides	490
CONCLUSIONS	493
ACKNOWLEDGMENTS	494
REFERENCES	494

11 Spectroscopic Techniques Applied to Uranium in Minerals

John M. Hanchar

INTRODUCTION	499
OPTICAL SPECTROSCOPIC METHODS	499
Absorption spectroscopy	500
Luminescence spectroscopy	505
X-RAY ABSORPTION SPECTROSCOPY	509
XAS spectroscopy of uranium in minerals	510
X-RAY PHOTOELECTRON SPECTROSCOPY	515
X-ray photoelectron spectroscopy of uranium in minerals	515
CONCLUDING COMMENTS	516
ACKNOWLEDGMENTS	516
REFERENCES	517

12 Infrared Spectroscopy and Thermal Analysis of the Uranyl Minerals

Jiří Čejka

INFRARED SPECTROSCOPY OF THE URANYL MINERALS	521
Introduction	521
Uranyl, UO_2^{2+}	523
Uranyl vibrational modes (fundamental vibrations)	523
Uranyl stretching vibrations, $\nu_1 \text{UO}_2^{2+}$ and $\nu_3 \text{UO}_2^{2+}$	524
Uranyl bending vibration $\nu_2 (\delta) \text{UO}_2^{2+}$	527
Estimating the uranyl (U-O_i) bond length from its stretching vibrations	527
Equatorial ligand effect on $\nu_3 \text{UO}_2^{2+}$	528
Anion vibrational modes (fundamental vibrations)	528
Molecular water, hydroxyl, hydroxonium and $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ vibrational modes (fundamental vibrations), hydrogen bonding and deuterioanalogues	530
Infrared spectra of:	
Uranyl oxide hydrates, alkali, alkaline-earth and other uranyl oxide hydrates	535
Uranyl silicates	543
Uranyl phosphates and arsenates	548

Table of Contents

Uranyl vanadates	557
Uranyl molybdates	560
Uranyl sulfates	562
Uranyl carbonates	567
Uranyl selenites and tellurites	576
Uranyl wolframates	578
THERMAL ANALYSIS OF THE URANYL MINERALS	578
Introduction	578
Thermal analysis of:	
Uranyl oxide hydrates, alkali, alkaline earth and other hydrates	582
Uranyl silicates	587
Uranyl phosphates and arsenates	590
Uranyl vanadates	598
Uranyl molybdates	600
Uranyl sulfates	601
Uranyl carbonates	604
Uranyl selenites and tellurites	607
Uranyl tungstates (wolframates)	608
ACKNOWLEDGMENTS	608
REFERENCES	608

13 Analytical Methods for Determination of Uranium in Geological and Environmental Materials

Stephen F. Wolf

INTRODUCTION	623
SAMPLE DISSOLUTION METHODS	623
Fluxed decomposition	624
Acid dissolution	624
CLASSICAL WET CHEMICAL TECHNIQUES	624
Gravimetric determination	625
Volumetric determination	625
Colorimetric determination	626
URANIUM SEPARATIONS	626
Coprecipitation	626
Liquid-liquid extraction	626
Ion-exchange	626
NUCLEAR METHODS	627
Radiometric techniques	627
α -Spectrometry	627
γ -Spectrometry	629
Neutron activation analysis	632
Fission track analysis	633
Instrumental neutron activation analysis	633
Radiochemical neutron activation analysis	634
ATOMIC SPECTROMETRIC TECHNIQUES	634
Atomic absorption spectrometry	635

Table of Contents

Atomic emission spectrometry	636
Flame emission spectrometry	637
Inductively coupled plasma-atomic emission spectrometry	637
Atomic fluorescence spectrometry	638
Fluorometry	638
Phosphorimetry	639
X-ray fluorescence	639
MASS SPECTROMETRY	640
Solid state mass spectrometry	641
Spark source mass spectrometry	641
Glow discharge mass spectrometry	641
Secondary ion mass spectrometry	641
Laser ablation mass spectrometry	641
Resonant ionization mass spectrometry	642
Thermal ionization mass spectrometry	642
Inductively coupled plasma mass spectrometry	642
Calibration methods	645
High resolution-inductively coupled plasma mass spectrometry	646
Isotope ratio determination	646
SUMMARY	647
ACKNOWLEDGMENTS	648
REFERENCES	648

14

Identification of Uranium-bearing Minerals and Inorganic Phases by X-ray Powder Diffraction

Frances C. Hill

INTRODUCTION	653
A BRIEF REVIEW OF X-RAY DIFFRACTION	653
POWDER DIFFRACTION DATA FOR URANIUM-BEARING PHASES	654
COMPARISON OF EXPERIMENTAL AND CALCULATED POWDER X-RAY DIFFRACTOGRAMS	656
SUMMARY	659
ACKNOWLEDGMENTS	659
APPENDIX TABLES: Formulas, Names, Space Groups, Lattice Parameters, and <i>d</i> -Spacings of the Five Most Prominent Powder Diffraction Peaks	662
REFERENCES	673