Contents

Preface xv

1. Elements 1

1.1 Introduction 1
1.2 A Brief History of the Solar System and Planet Earth 2
1.3 The Composition of Earth's Crust and Soils 3
1.4 The Abundance of Elements in the Solar System, Earth's Crust, and Soils 3
1.5 Elements and Isotopes 4
1.6 Nuclear Binding Energy 6
1.7 Enrichment and Depletion during Planetary Formation 8
1.8 Planetary Accretion 9
1.9 The Rock Cycle 12
1.10 Soil Formation 13
1.11 Concentration Frequency Distributions of the Elements 16
1.12 Estimating the Most Probable Concentration and Concentration Range Using the Logarithmic Transformation 18
1.13 Summary 21
Appendix 1A Factors Governing Nuclear Stability and Isotope Abundance 22
1A.1 The Table of Isotopes and *Nuclear Magic Numbers* 22
1A.2 Nuclear Magic Numbers 22
Appendix 1B Nucleosynthesis 25
1B.1 Nuclear Reactions 25
1B.2 Nuclear Fusion 26
1B.3 Neutron Capture 28
1B.4 Cosmic Ray Spallation 30
1B.5 Transuranium Elements 30
Appendix 1C Thermonuclear Fission Cycles 32
1C.1 The CNO Cycle 32
1C.2 The Triple-Alpha Process 33
1C.3 Carbon Burning 34
Appendix 1D Neutron-Emitting Reactions that Sustain the *S-Process* 34
Appendix 1E Random Sequential Dilutions and the Law of Proportionate Effect 35
Appendix 1F The Estimate of Central Tendency and Variation of a Log-Normal Distribution 37

2. Soil Moisture and Hydrology 41

2.1 Introduction 41
2.2 Water Resources and the Hydrologic Cycle 42
2.3 Water Budgets 43
2.4 Residence Time and Runoff Ratios 43
2.5 Groundwater Hydrology 45
2.5.1 Water in the Porosphere 45
2.5.2 Hydrologic Units 47
2.5.3 Darcy's Law 48
2.5.4 Hydrostatic Heads and Hydrostatic Gradients 49
2.5.5 Intrinsic Permeability 54
2.5.6 Groundwater Flow Nets 56
2.6 Vadose Zone Hydrology 58
2.6.1 Capillary Forces 58
2.6.2 Soil Moisture Zones 60
2.6.3 The Water Characteristic Curve and Vadose Zone Hydraulic Conductivity 62
2.7 Elementary Solute Transport Models 62
2.7.1 The Retardation Coefficient Model 62
2.7.2 Plate Theory: Multiple Sequential Partitioning 65
2.8 Summary 71
Appendix 2A Soil Moisture Recharge and Loss 71
Appendix 2B The Water-Holding Capacity of a Soil Profile 72
Appendix 2C Predicting Capillary Rise 75
Appendix 2D Symbols and Units in the Derivation of the Retardation Coefficient Model of Solute Transport 76
Appendix 2E Symbols and Units in the Derivation of the Plate Theory Model of Solute Transport 77
Appendix 2F Empirical Water Characteristic Function and Unsaturated Hydraulic Conductivity 79

3. Clay Mineralogy and Clay Chemistry 85

3.1 Introduction 85
3.2 Mineral Weathering 86
3.2.1 Mineralogy 86
3.3 The Structure of Layer Silicates 89
3.3.1 Coordination Polyhedra 90
3.3.2 The Phyllosilicate Tetrahedral Sheet 91
3.3.3 The Phyllosilicate Octahedral Sheet 92
3.3.4 Kaolinite Layer Structure 93
3.3.5 Talc Layer Structure 93
3.3.6 Mica-Illite Layer Structure 94
3.3.7 Chlorite and Hydroxy-Interlayered Smectite Layer Structure 96
3.3.8 Layer Structure of the Swelling Clay Minerals: Smectite and Vermiculite 97
Appendix 3A Formal Oxidation Numbers 104

Appendix 3B The Geometry of Pauling's Radius Ratio Rule 105
Appendix 3C Bragg's Law and X-Ray Diffraction in Layer Silicates 109
Appendix 3D Osmotic Model of Interlayer Swelling Pressure 109
Appendix 3E Experimental Estimates of Interlayer Swelling Pressure 111

4. Ion Exchange 117

4.1 Introduction 117
4.2 The Discovery of Ion Exchange 118
4.3 Ion Exchange Experiments 119
4.3.1 Preparing Clay Saturated with a Single Cation 119
4.3.2 Measuring Cation Exchange Capacity 120
4.3.3 Measuring the Cation Exchange Isotherm 120
4.3.4 Selectivity Coefficients and the Exchange Isotherm 122
4.4 Interpreting the Ion Exchange Isotherm 125
4.4.1 The Ion Exchange Isotherm for Symmetric Exchange 126
4.4.2 The Ion Exchange Isotherm for Asymmetric Exchange 127
4.4.3 Effect of Ionic Strength on the Ion Exchange Isotherm 129
4.4.4 Effect of Ion Selectivity on the Ion Exchange Isotherm 131
4.4.5 Other Influences on the Ion Exchange Isotherm 138
4.5 Summary 140
Appendix 4A Thermodynamic and Conditional Selectivity Coefficients 142
Appendix 4B Nonlinear Least Square Fitting of Exchange Isotherms 143
Appendix 4C Equivalent Fraction-Dependent Selectivity Coefficient for (Mg^{2+}, Ca^{2+}) Exchange on the Libby Vermiculite 144

5. Water Chemistry 151

5.1 The Equilibrium Constant 151
5.1.1 Thermodynamic Functions for Chemical Reactions 151
5.1.2 Gibbs Energy of Reaction and the Equilibrium Constant 152
5.2 Activity and the Equilibrium Constant 153
5.2.1 Concentrations and Activity 153
5.2.2 Ionic Strength *I* 154
5.2.3 Empirical Ion Activity Coefficient Expressions 154
5.3 Modeling Water Chemistry 156
5.3.1 Simple Equilibrium Systems 156
5.3.2 Water Chemistry Simulations 170
5.3.3 Modeling the Chemistry of Environmental Samples: Groundwater, Soil Pore Water, and Surface Water 179
5.4 Summary 187
Appendix 5A ChemEQL Result Data File Format 187
Appendix 5B Validating Water Chemistry Simulations 188
Appendix 5C Validation Assessment for Examples 5.13 and 5.16 193
Example 5.13: Gypsum Solubility 193
Example 5.16: Gibbsite Solubility 194
Appendix 5D Cinnabar Solubility in an Open System Containing the Gas Dihydrogen Sulfide 196

Appendix 5E Simultaneous Calcite-Apatite-Pyromorphite Solubility 199
Appendix 5F Simultaneous Gibbsite-Variscite Solubility 200
Appendix 5G Apatite Solubility as a Function of pH 200
Appendix 5H Effect of the Citrate on the Solubility of the Calcium Phosphate Mineral Apatite 201
Appendix 5I Effect of the Fungal Siderophore *Desferrioxamine B* on the Solubility of the Iron Oxyhydroxide Goethite 203

6. Natural Organic Matter and Humic Colloids 209

6.1 Introduction 209
6.2 Soil Carbon Cycle 209
6.2.1 Carbon Fixation 210
6.2.2 Carbon Mineralization 212
6.2.3 Oxidation of Organic Compounds by Dioxygen 213
6.3 Soil Carbon 217
6.3.1 Carbon Turnover Models 217
6.3.2 Soil Carbon Pools 221
6.4 Dissolved Organic Carbon 223
6.4.1 Organic Acids 223
6.4.2 Amino Acids 224
6.4.3 Extracellular Enzymes 224
6.4.4 Siderophores 224
6.4.5 Biosurfactants 228
6.5 Humic Substances 229
6.5.1 Extraction and Fractionation 229
6.5.2 Elemental Composition 230
6.5.3 Chemical Composition 231
6.6 Humic Colloids 245
6.7 Summary 246
Appendix 6A Hydroxamate and Catecholamide Siderophore Moieties 247
Appendix 6B Surface Microlayers 250
Appendix 6C Humic Oxygen Content and Titratable Weak Acids 252
Appendix 6D Hydrophobic and Hydrophilic Colloids 252

7. Acid-Base Chemistry 257

7.1 Introduction 257
7.2 Principles of Acid-Base Chemistry 258
7.2.1 Dissociation: The Arrhenius Model of Acid-Base Reactions 258
7.2.2 Hydrogen Ion Transfer: The Brønsted-Lowery Model of Acid-Base Reactions 259
7.2.3 Conjugate Acids and Bases 259
7.2.4 Defining Acid and Base Strength 260
7.2.5 Water Reference Level 261
7.2.6 The Aqueous Carbon Dioxide Reference Level 262
7.3 Sources of Environmental Acidity and Basicity 263
7.3.1 Chemical Weathering of Rocks and Minerals 265

7.3.2 Silicate Rocks 265
7.3.3 Carbonate Rocks 267
7.3.4 Sulfide Minerals 268
7.3.5 Evaporite Rocks 269
7.4 Atmospheric Gases 269
7.4.1 Carbon Dioxide: Above Ground 269
7.4.2 Carbon Dioxide: Below Ground 271
7.4.3 Sulfur Oxides 271
7.4.4 Nitrogen Oxides 273
7.5 Ammonia-Based Fertilizers and Biomass Harvesting 276
7.6 Charge Balancing in Plant Tissue and the Rhizosphere 278
7.6.1 Water Alkalinity 280
7.6.2 Carbonate Alkalinity 281
7.6.3 Silicate Alkalinity 281
7.6.4 The Methyl Orange End-Point 282
7.6.5 Mineral Acidity 283
7.7 Mechanical Properties of Clay Colloids and Soil Sodicity 283
7.7.1 Clay Plasticity and Soil Mechanical Properties 284
7.7.2 Clay Content and Granular Particle Contacts 286
7.7.3 Sodicity 288
7.7.4 Sodium-Ion Accumulation on the Clay Exchange Complex: ESP 289
7.7.5 Pore Water Electrical Conductivity EC_w 292
7.7.6 Extreme Alkalinity: Soil pH>8.4 293
7.7.7 Predicting Changes in Pore Water SAR 296
7.8 Exchangeable Acidity 298
7.8.1 Exchangeable Calcium and Soil Alkalinity 298
7.8.2 Gibbsite Solubility 298
7.8.3 The Role of Asymmetric (Al^{3+}, Ca^{2+}) Exchange 300
7.8.4 Neutralizing Exchangeable Soil Acidity 301
7.9 Summary 302
Appendix 7A Buffer Index 303
Appendix 7B Converting Mass Fraction to Sum-of-Oxides Composition 305
Appendix 7C Saturation Effect: Atmospheric Conversion of Sulfur Trioxide to Sulfuric Acid 305
Appendix 7D Bicarbonate and Carbonate Reference Levels 306
Appendix 7E Calculating the pH of a Sodium Carbonate Solution 308
Appendix 7F Calculating the Aqueous Carbon Dioxide Concentration in a Weak Base Solution 309
Appendix 7G Ion Exchange Isotherm for Asymmetric (Ca^{2+}, Al^{3+}) Exchange 310
Appendix 7H The Effect of (Na^{+}, Ca^{2+}) Exchange on the Critical Coagulation Concentration of Montmorillonite 313
Appendix 7I Predicting Changes in SAR by Water Chemistry Simulation 316

8. Redox Chemistry 321

8.1 Introduction 321
8.2 Redox Principles 322
8.2.1 Formal Oxidation Numbers 322
8.2.2 Balancing Reduction Half Reactions 324
8.2.3 Reduction Half Reactions and Electrochemical Cells 326
8.2.4 The Nernst Equation 327
8.3 Interpreting Redox Stability Diagrams 331
8.3.1 Environmental Redox Conditions 331
8.3.2 Measuring Environmental Reduction Potentials Using Platinum Oxidation-Reduction Electrodes 333
8.3.3 Pourbaix Stability Diagrams: Preparation and Interpretation 334
8.3.4 Water Stability Limits 334
8.3.5 The Solute-Solute Reduction Boundary 336
8.3.6 The Solute-Solute Hydrolysis Boundary 338
8.3.7 The Solute-Precipitate Boundary 339
8.3.8 The Solute-Precipitate Reduction Boundary 340
8.3.9 The Precipitate-Precipitate Reduction Boundary 341
8.3.10 Simple Rules for Interpreting Pourbaix Diagrams 343
8.4 Microbial Respiration and Electron Transport Chains 345
8.4.1 Catabolism and Respiration 347
8.4.2 Electron Transport Chains 349
8.4.3 Environmental Redox Conditions and Microbial Respiration 360
8.5 Summary 361
Appendix 8A Assigning Formal Oxidation Numbers 362
Appendix 8B Converting (*pe, pH*) Redox Coordinates into (E_H, *pH*) Coordinates 363
Appendix 8C Limitations in the Measurement of the Environmental Reduction Potential Using Platinum *ORP* Electrodes 365

9. Adsorption and Surface Chemistry 371

9.1 Introduction 371
9.2 Mineral and Organic Colloids as Environmental Adsorbents 372
9.3 The Adsorption Isotherm Experiment 374
9.4 Hydrophobic and Hydrophilic Colloids 379
9.5 Interpreting the Adsorption Isotherm Experiment 379
9.5.1 The Langmuir Adsorption Model 380
9.5.2 Ion Exchange Adsorption Isotherms 382
9.5.3 Linear Adsorption or Partitioning Model 383
9.6 Variable-Charge Mineral Surfaces 387
9.7 The Adsorption Envelope Experiment: Measuring pH-Dependent Ion Adsorption 388
9.7.1 Adsorption Edges 389
9.7.2 Measuring pH-Dependent Surface Charge 390
9.7.3 Proton Surface Charge Sites 391

9.8 Valence Bond Model of Proton Sites 392
9.8.1 Interpreting pH-Dependent Ion Adsorption Experiments 394
9.9 Surface Complexes 395
9.10 Summary 399
Appendix 9A Particle Sedimentation Rates in Water: Stokes's Law 400
Appendix 9B Linear Langmuir Expression 401
Appendix 9C Hydrolysis Model of Proton Sites 402

10. Risk Assessment 409

10.1 Introduction 409
10.2 The Federal Risk Assessment Paradigm 411
10.2.1 Risk Assessment 411
10.2.2 Risk Management and Mitigation 411
10.3 Dose-Response Assessment 411
10.3.1 Dose-Response Distributions 412
10.3.2 The No-Threshold One-Hit Model 413
10.3.3 Low-Dose Extrapolation of Noncarcinogenic Response Functions 414
10.3.4 Estimating the Steady-State Body Burden 415
10.3.5 Reference Dose *RfD* 416
10.3.6 Low-Dose Extrapolation of Carcinogenic Response Functions 416
10.4 Exposure Pathway Assessment 419
10.4.1 Receptors 419
10.4.2 Exposure Routes 420
10.4.3 Exposure Points 422
10.4.4 Fate and Transport 423
10.4.5 Primary and Secondary Sources 424
10.4.6 Exposure Assessment 425
10.5 Intake Estimates 425
10.5.1 Averaging Time 425
10.5.2 Exposure Factors 427
10.6 Risk Characterization 428
10.6.1 The Incremental Excess Lifetime Cancer Risk 428
10.6.2 The Hazard Quotient 430
10.7 Exposure Mitigation 431
10.8 Summary 434
Appendix 10A Chemical- and Site-Specific Factors that May Affect Contaminant Transport by Surface Water 435
Appendix 10B Chemical- and Site-Specific Factors that May Affect Contaminant Transport by Groundwater 436
Appendix 10C Chemical- and Site-Specific Factors that May Affect Contaminant Transport Involving Soils or Sediments 437
Appendix 10D Chemical- and Site-Specific Factors that May Affect Contaminant Transport Involving Air and Biota 438
Appendix 10E The Water Ingestion Equation 438

Appendix 10F Soil Ingestion Equation 441
Appendix 10G Food Ingestion Equation 442
Appendix 10H Air Inhalation Equation 442
Appendix 10I Hazard Index—Cumulative Noncarcinogenic Risk 443
Appendix 10J Cumulative Target Risk—Cumulative Noncarcinogenic Risk 444
References 449
Index 463