Contents

LIST OF EXAMPLES XII

NOTATION XV

1 INTRODUCTION TO GROUNDWATER GEOCHEMISTRY 1
1.1 Groundwater as drinking water 1
1.1.1 Standards for drinking water 1
1.2 Units of analysis 3
1.3 Groundwater quality 7
1.4 Sampling of groundwater 10
1.4.1 Depth integrated or depth specific sampling 10
1.4.2 Procedures for sampling of groundwater 12
1.5 Chemical analysis of groundwater 15
1.5.1 Field analyses and sample conservation 15
1.5.2 Accuracy of chemical analysis 17
Problems 20
References 21

2 FROM RAINWATER TO GROUNDWATER 23
2.1 The hydrological cycle 23
2.2 The composition of rainwater 26
2.2.1 Sources and transport of atmospheric pollutants 31
2.3 Stable isotopes in rain 31
2.3.1 Isotopic ratios and the δ notation 32
2.3.2 The Rayleigh process 33
2.3.3 The isotopic composition of rain 37
2.4 Dry deposition and evapotranspiration 41
2.5 Mass balances and ecosystem dynamics 46
2.5.1 Water quality profiles in the unsaturated soil 49
2.6 Overall controls on water quality 51
Problems 58
References 59

3 FLOW AND TRANSPORT 63
3.1 Flow in the unsaturated zone 63
3.2 Flow in the saturated zone 64

3.2.1 Darcy's law 64
3.2.2 Flowlines in the subsoil 67
3.2.3 Effects of non-homogeneity 70
3.2.4 The aquifer as a chemical reactor 71
3.3 Dating of groundwater 72
3.4 Retardation 75
3.4.1 The retardation equation 76
3.4.2 Indifferent and broadening fronts 79
3.4.3 Sharpening fronts 82
3.4.4 Solid and solute concentrations 84
3.5 Diffusion 86
3.5.1 Diffusion coefficients 87
3.5.2 Diffusion as a random process 89
3.5.3 Diffusive transport 93
3.5.4 Isotope diffusion 96
3.6 Dispersion 99
3.6.1 Column breakthrough curves 102
3.6.2 Dispersion coefficients and dispersivity 105
3.6.3 Macrodispersivity 107
Problems 113
References 115

4 MINERALS AND WATER 119
4.1 Equilibria and the solubility of minerals 119
4.2 Corrections for solubility calculations 123
4.2.1 Concentration and activity 123
4.2.2 Aqueous complexes 127
4.2.3 Combined complexes and activity corrections 128
4.2.4 Calculation of saturation states 131
4.3 Mass action constants and thermodynamics 132
4.3.1 The calculation of mass action constants 132
4.3.2 Calculation of mass action constants at different temperature 133
4.4 Equilibrium calculations with PHREEQC 135
4.4.1 Speciation calculations using PHREEQC 135
4.4.2 The PHREEQC database 137
4.4.3 Mineral equilibration 141
4.5 Solid solutions 142
4.5.1 Basic theory 142
4.5.2 The fractionation factor for solid solutions 148
4.5.3 Kinetic effects on the fractionation factor 149
4.6 Kinetics of geochemical processes 152
4.6.1 Kinetics and equilibrium 152
4.6.2 Chemical reactions and rates 153
4.6.3 Temperature dependency of reaction rates 159
4.6.4 Mechanisms of dissolution and crystallization 160
4.6.5 Rate laws for mineral dissolution and precipitation 162
Problems 169
References 171

5 CARBONATES AND CARBON DIOXIDE 175
5.1 Carbonate minerals 176
5.2 Dissolved carbonate equilibria 178
5.2.1 The carbonic acid system 179
5.2.2 Determining the carbonate speciation in groundwater 183
5.3 Carbon dioxide in soils 186
5.4 Calcite solubility and P_{CO_2} 191
5.4.1 Calcite dissolution in systems open and closed for CO_2 gas 193
5.4.2 Two field examples 195
5.5 Carbonate rock aquifers 197
5.5.1 Dolomite and dedolomitization 201
5.5.2 Pleistocene carbonate aquifers 205
5.6 Kinetics of carbonate reactions 210
5.6.1 Dissolution 210
5.6.2 Precipitation 217
5.7 Carbon isotopes 218
5.7.1 Carbon-13 trends in aquifers 221
5.7.2 ^{14}C and groundwater age 226
5.7.3 Retardation by sorption and stagnant zone diffusion 228
Problems 232
References 236

6 ION EXCHANGE 241
6.1 Cation exchange at the salt/fresh water interface 242
6.2 Adsorbents in soils and aquifers 247
6.2.1 Clay minerals 248
6.3 Exchange equations 251
6.3.1 Values for exchange coefficients 254
6.3.2 Calculation of exchanger composition 255
6.3.3 Calculation of exchanger composition with PHREEQC 257
6.3.4 Determination of exchangeable cations 260
6.4 Chromatography of cation exchange 262
6.4.1 Field examples of freshening 263
6.4.2 Salinity effects on cation exchange 268
6.4.3 Quality patterns with salinization 271
6.4.4 Fronts and chromatographic sequences 272
6.4.5 Modeling chromatographic sequences with PHREEQC 275
6.5 Physical non-equilibrium 283
6.5.1 Modeling stagnant zones 285
6.6 The Gouy-Chapman theory of the double layer 288
6.6.1 Numerical integration of the double layer equations 293
6.6.2 Practical aspects of double layer theory 296
6.7 Irrigation water quality 299
Problems 303
References 306

7 SORPTION OF TRACE METALS 311
7.1 The origin and occurrence of heavy metals in groundwater 311
7.2 Sorption isotherms and distribution coefficients 315

7.2.1 Distribution coefficients from ion exchange 318
7.3 Variable charge surfaces 322
7.3.1 Titration curves with suspended oxide particles 322
7.3.2 Surface charge and point of zero charge, *PZC* 324
7.3.3 Sorption edges 328
7.3.4 Sorption, absorption, and coprecipitation 333
7.4 Surface complexation 334
7.4.1 Surface complexation models 338
7.4.2 The ferrihydrite ($Fe(OH)_3$) database 340
7.4.3 Diffuse double layer concentrations in surface complexation models 343
7.5 Complexation to humic acids 344
7.5.1 The ion association model 346
7.5.2 Tipping and Hurley's discrete site model "WHAM" 348
7.5.3 Distribution models 354
7.5.4 Humic acids as carriers of trace elements 356
7.6 Kinetics of surface complexation 358
7.6.1 Extrapolation of adsorption kinetics for other metal ions 363
7.7 Field applications 363
Problems 367
References 369

8 SILICATE WEATHERING 375
8.1 Weathering processes 375
8.2 The stability of weathering products 380
8.3 Incongruent dissolution of primary silicates 383
8.4 The mass balance approach to weathering 389
8.5 Kinetics of silicate weathering 395
8.6 Field weathering rates 400
8.7 Acid groundwater 404
8.7.1 Buffering processes in aquifers 405
Problems 410
References 412

9 REDOX PROCESSES 415
9.1 Basic theory 415
9.1.1 The significance of redox measurements 420
9.1.2 Redox reactions and the pe concept 422
9.2 Redox diagrams 423
9.2.1 Stability of water 424
9.2.2 The stability of dissolved species and gases: Arsenic 425
9.2.3 The stability of minerals in redox diagrams 432
9.3 Sequences of redox reactions and redox zoning 438
9.3.1 Decomposition of organic matter 442
9.4 Oxygen consumption 446
9.4.1 Pyrite oxidation 450
9.4.2 Kinetics of pyrite oxidation 450
9.4.3 Oxygen transport and pyrite oxidation 453
9.5 Nitrate reduction 458
9.5.1 Nitrate reduction by organic matter oxidation 459
9.5.2 Nitrate reduction by pyrite and ferrous iron 462

9.6 Iron reduction and sources of iron in groundwater 465
9.6.1 Iron in aquifer sediments 465
9.6.2 Reductive dissolution of iron oxides 466
9.7 Sulfate reduction and iron sulfide formation 472
9.7.1 The formation of iron sulfides 476
9.8 The formation of methane 477
Problems 479
References 480

10 POLLUTION BY ORGANIC CHEMICALS 489
10.1 Gas-water exchange 489
10.1.1 Evaporation of a pure organic liquid 494
10.2 Transport of pure organic liquids through soil 496
10.3 Sorption of organic chemicals 499
10.3.1 Sorption of charged organic molecules 504
10.3.2 Sorption in stagnant zones 506
10.3.3 Release from stagnant zones and blobs 510
10.4 Transformation reactions of organic chemicals 516
10.4.1 Monod biotransformation kinetics 518
10.5 Kinetic complexation of heavy metals on organics 529
Problems 535
References 537

11 NUMERICAL MODELING 541
11.1 Numerical modeling of transport 543
11.1.1 Only diffusion 543
11.1.2 Advection and diffusion/dispersion 550
11.1.3 Non-linear reactions 558
11.2 Examples of hydrogeochemical transport modeling 560
11.2.1 Tritium-Helium age dating 561
11.2.2 Toluene degradation in an aquifer 565
11.2.3 Remediation of a BTEX polluted site 568
11.2.4 Acid drainage from a Uranium mine 570
11.2.5 In-situ iron removal from groundwater 579
11.2.6 Arsenic in Bangladesh groundwater 585
11.2.7 Fractionation of isotopes 590
References 595

APPENDIX A: HYDROGEOCHEMICAL MODELING WITH PHREEQC 599

APPENDIX B: ANSWERS TO PROBLEMS 617

INDEX 635