

*Environmental and Low Temperature Geochemistry* presents the conceptual and quantitative principles of geochemistry in order to foster an understanding of natural processes at and near the Earth's surface, as well as anthropogenic impacts on the natural environment. It provides the reader with the essentials of concentration, speciation and reactivity of elements in soils, waters, sediments and air, drawing attention to both thermodynamic and kinetic controls. Specific features include:

- An introductory chapter that reviews basic chemical principles applied to environmental and low-temperature geochemistry
- Explanation and analysis of the importance of minerals in the environment
- Principles of aqueous geochemistry
- Organic compounds in the environment
- The role of microbes in processes such as biomineralization, elemental speciation and reduction-oxidation reactions
- Thorough coverage of the fundamentals of important geochemical cycles (C, N, P, S)
- Atmospheric chemistry
- Soil geochemistry
- The roles of stable isotopes in environmental analysis
- Radioactive and radiogenic isotopes as environmental tracers and environmental contaminants
- Principles and examples of instrumental analysis in environmental geochemistry

The text concludes with a case study of surface water and groundwater contamination that includes interactions and reactions of naturally derived inorganic substances and introduced organic compounds (fuels and solvents), and illustrates the importance of interdisciplinary analysis in environmental geochemistry.

*Readership:* Advanced undergraduate and graduate students studying environmental/low T geochemistry as part of an earth science, environmental science or related program.

**Peter Crowley Ryan** is Professor of Geology and Environmental Studies at Middlebury College where he teaches courses in environmental geochemistry, hydrology, sedimentary geology and interdisciplinary environmental science. He received a Ph.D. in geology at Dartmouth College, an M.S. in geology from the University of Montana and a B.A. in earth sciences from Dartmouth College. He has served as Director of the Program in Environmental Studies and as Chair of the Department of Geology at Middlebury College. His research interests fall into two main areas: (1) understanding the geological and mineralogical controls on trace-element speciation, particularly the occurrence and mobility of arsenic and uranium in bedrock aquifers; and (2) the temporal evolution of marine terrace soils in the tropics, with emphasis on mechanisms and rates of mineralogical reactions, nutrient cycling and application of soil geochemical analysis to correlation and geological interpretation.



[www.wiley.com/go/ryan/geochemistry](http://www.wiley.com/go/ryan/geochemistry)

**WILEY Blackwell**



Also available  
as an e-book

ISBN: 978-1-4051-8612-4



9 781405 186124

Acknowledgements, xii

About the Companion Website, xiii

## **1 BACKGROUND AND BASIC CHEMICAL PRINCIPLES: ELEMENTS, IONS, BONDING, REACTIONS, 1**

- 1.1 An overview of environmental geochemistry – history, scope, questions, approaches, challenges for the future, 1
- 1.2 The naturally occurring elements – origins and abundances, 2
- 1.3 Atoms and isotopes: a brief review, 6
- 1.4 Measuring concentrations, 8
  - 1.4.1 Mass-based concentrations, 8
  - 1.4.2 Molar concentrations, 9
  - 1.4.3 Concentrations of gases, 10
  - 1.4.4 Notes on precision and accuracy, significant figures and scientific notation, 10
- 1.5 Periodic table, 11
- 1.6 Ions, molecules, valence, bonding, chemical reactions, 14
  - 1.6.1 Ionic bond strength, 14
  - 1.6.2 Covalent bonds, 16
  - 1.6.3 Electronegativity, 17
  - 1.6.4 Metallic bonds, hydrogen bonds and van der Waals forces, 18
- 1.7 Acid–base equilibria, pH, K values, 19
- 1.8 Fundamentals of redox chemistry and chemical reactions, 21

- 1.9 Chemical reactions, 23
- 1.10 Equilibrium, thermodynamics and driving forces for reactions: systems, gibbs energies, enthalpy and heat capacity, entropy, volume, 23
  - 1.10.1 Systems, species, phases and components, 24
  - 1.10.2 First law of thermodynamics, 26
  - 1.10.3 Second law of thermodynamics, 27
  - 1.10.4 Enthalpy, 27
  - 1.10.5 Heat capacity, 29
  - 1.10.6 Gibbs free energy, 30
  - 1.10.7 Gibbs free energy and the equilibrium constant, 31
- 1.11 Kinetics and reaction rates: distance from equilibrium, activation energy, metastability, 33
  - 1.11.1 Reaction rate, reaction order, 34
  - 1.11.2 Temperature and the Arrhenius equation, 36
- Review questions, 37
- References, 37

## **2 SURFICIAL AND ENVIRONMENTAL MINERALOGY, 39**

- 2.1 Introduction to minerals and unit cells, 40
- 2.2 Ion coordination, Pauling's rules and ionic substitution, 42
  - 2.2.1 Coordination and radius ratio, 42

- 2.2.2 Bond-strength considerations, 45
- 2.2.3 Pauling's and Goldschmidt's rules of ionic solids, 45
- 2.3 Silicates, 48
  - 2.3.1 Nesosilicates, 49
  - 2.3.2 Inosilicates, 50
  - 2.3.3 Phyllosilicates, 52
  - 2.3.4 Tectosilicates, 58
- 2.4 Clay minerals (T–O minerals, T–O–T minerals, interstratified clays), 58
  - 2.4.1 Smectite, 59
  - 2.4.2 Smectites with tetrahedrally derived layer charge, 60
  - 2.4.3 Smectites with octahedrally derived layer charge, 60
  - 2.4.4 Vermiculite, 62
  - 2.4.5 Illite, 62
  - 2.4.6 Chlorite and Berthierine, 63
  - 2.4.7 Kaolin (kaolinite and halloysite), 63
  - 2.4.8 Interstratified clay minerals, 64
  - 2.4.9 Trace metals and metalloids in clay minerals, 64
- 2.5 Crystal chemistry of adsorption and cation exchange, 64
  - 2.5.1 Cation exchange, 66
  - 2.5.2 Double-layer complexes, 68
- 2.6 Low-temperature non-silicate minerals: carbonates, oxides and hydroxides, sulfides, sulfates, salts, 70
  - 2.6.1 Carbonates, 70
  - 2.6.2 Oxides and hydroxides, 71
  - 2.6.3 Sulfides and sulfates, 72
  - 2.6.4 Halide and nitrate salts, 74
- 2.7 Mineral growth and dissolution, 74
- 2.8 Biomineralization, 78
- Review questions, 79
- References, 80

### 3 ORGANIC COMPOUNDS IN THE ENVIRONMENT, 82

- 3.1 Introduction to organic chemistry: chains and rings, single, double, and triple bonds, functional groups, classes of organic compounds, organic nomenclature, 82
  - 3.1.1 Definition of organic compounds, 82
  - 3.1.2 Hybridization of carbon atoms in organic compounds, 83
  - 3.1.3 Alkanes, 84
  - 3.1.4 Alkenes, 86
  - 3.1.5 Functional groups, 86
  - 3.1.6 Aromatic hydrocarbons and related compounds, 88
  - 3.1.7 Nitrogen, phosphorus and sulfur in organic compounds, 92
  - 3.1.8 Pharmaceutical compounds, 93
- 3.2 Natural organic compounds at the earth surface, 94
  - 3.2.1 Fossil fuels, 95
- 3.3 Fate and transport of organic pollutants, controls on bioavailability, behavior of DNAPLs and LNAPLs, biodegradation, remediation schemes, 96
  - 3.3.1 Solid–liquid–gas phase considerations, 96
  - 3.3.2 Solubility considerations, 97
  - 3.3.3 Interactions of organic compounds and organisms, 98
  - 3.3.4 Adsorption of organic compounds, 99
  - 3.3.5 Non-aqueous phase liquids (NAPLs) in the environment, 103
  - 3.3.6 Biodegradation, 104

3.3.7 Remediation, 105

3.4 Summary, 106

Questions, 106

References, 106

## **4 AQUEOUS SYSTEMS – CONTROLS ON WATER CHEMISTRY, 108**

4.1 Introduction to the geochemistry of natural waters, 108

4.1.1 Geochemistry and the hydrologic cycle, 108

4.2 The structure of water – geometry, polarity and consequences, 113

4.3 Dissolved versus particulate: examples of solutions and suspensions, 114

4.3.1 Dissolved vs. particulate vs. colloidal, 115

4.4 Speciation: simple ions, polyatomic ions and aqueous complexes, 116

4.5 Controls on the solubility of inorganic elements and ions, 117

4.5.1 The ratio of ionic charge: ionic radius and its effect on solubility, 119

4.5.2 Reduction–oxidation reactions, 120

4.5.3 Half-cell reactions, 120

4.5.4 Redox reactions in the environment, 122

4.5.5 pH and acid–base consideration, 123

4.5.6 Ligands and elemental mobility, 124

4.6 Ion activities, ionic strength, TDS, 125

4.6.1 Ion activity product, 126

4.6.2 Ionic strength, 126

4.6.3 Total dissolved solids, 126

4.7 Solubility products, saturation, 127

4.8 Co-precipitation, 128

4.9 Behavior of selected elements in aqueous systems, 129

4.9.1 Examples of heavy metals and metalloids, 129

4.9.2 Eh–pH diagrams, 132

4.9.3 Silicon in solutions, 136

4.10 Effect of adsorption and ion exchange on water chemistry, 137

4.10.1 Ionic potential, hydration radius and adsorption, 138

4.10.2 Law of mass action and adsorption, 138

4.10.3 Adsorption edges, 140

4.10.4 Adsorption isotherms, 142

4.11 Other graphical representations of aqueous systems: piper and stiff diagrams, 143

4.12 Summary, 146

Questions, 147

References, 147

## **5 CARBONATE GEOCHEMISTRY AND THE CARBON CYCLE, 149**

5.1 Carbonate geochemistry: inorganic carbon in the atmosphere and hydrosphere, 149

5.1.1 Atmospheric CO<sub>2</sub>, carbonate species and the pH of rain, 150

5.1.2 Speciation in the carbonate system as a function of pH, 151

5.1.3 Alkalinity, 152

5.1.4 Carbonate solubility and saturation, 155

5.1.5 The effect of CO<sub>2</sub> partial pressure on stability of carbonate minerals, 157

5.1.6 The effect of mineral composition on stability of carbonate minerals, 157

5.2 The carbon cycle, 158

5.2.1 Oxidation states of carbon, 158

5.2.2 Global-scale reservoirs and fluxes of carbon, 159

5.2.3 Fixation of carbon into the crust, 161

5.2.4 Rates of flux to and from the crust, 164

- 5.2.5 The ocean reservoir, 166
- 5.2.6 Fixation of C into oceans, 166
- 5.2.7 Long-term viability of oceans as C sink, 168
- 5.2.8 The atmospheric reservoir, 171
- 5.2.9 Sequestration, 174

Questions, 175

References, 176

## **6 BIOGEOCHEMICAL CYCLES – N, P, S, 177**

- 6.1 The nitrogen cycle, 180
  - 6.1.1 Nitrogen valence, nitrogen species, 181
  - 6.1.2 Processes operating within the nitrogen cycle, 182
  - 6.1.3 Global scale reservoirs and fluxes of nitrogen, 184
  - 6.1.4 Human perturbation of the nitrogen cycle and resulting environmental impacts, 186
- 6.2 The phosphorus cycle, 190
  - 6.2.1 P cycling in soils, 191
  - 6.2.2 The global phosphorus cycle, 193
  - 6.2.3 Phosphorus and eutrophication, 194
- 6.3 Comparison of N and P, 195
- 6.4 The sulfur cycle, 196
  - 6.4.1 Sulfur valence, sulfur species, 196
  - 6.4.2 The global S cycle, 197
  - 6.4.3 The marine S cycle, 198
  - 6.4.4 Soils and biota, 200
  - 6.4.5 Atmosphere, 200
  - 6.4.6 River flux, 201
- 6.5 Integrating the C, N, P and S cycles, 202

Questions, 203

References, 203

## **7 THE GLOBAL ATMOSPHERE: COMPOSITION, EVOLUTION AND ANTHROPOGENIC CHANGE, 206**

- 7.1 Atmospheric structure, circulation and composition, 206
  - 7.1.1 Structure and layering of the atmosphere, 207
  - 7.1.2 Geological record of atmospheric composition, 208
  - 7.1.3 Climate proxies, 209
  - 7.1.4 Orbital control on C, 210
  - 7.1.5 Composition of the current atmosphere, 213
  - 7.1.6 Air circulation, 214
- 7.2 Evaporation, distillation, CO<sub>2</sub> dissolution and the composition of natural precipitation, 218
- 7.3 The electromagnetic spectrum, greenhouse gases and climate, 219
  - 7.3.1 Electromagnetic spectrum, 219
  - 7.3.2 Re-radiation from earth surface, 219
  - 7.3.3 Greenhouse effect and heat trapping, 222
- 7.4 Greenhouse gases: structures, sources, sinks and effects on climate, 223
  - 7.4.1 Molecular structures and vibrations of greenhouse gases, 223
  - 7.4.2 Greenhouse gases, radiative forcing, GWPs, 224
  - 7.4.3 Global warming, 227

Questions, 228

References, 228

## **8 URBAN AND REGIONAL AIR POLLUTION, 230**

- 8.1 Oxygen and its impact on atmospheric chemistry, 231
- 8.2 Free radicals, 232
- 8.3 Sulfur dioxide, 234

- 8.4 Nitrogen oxides, 237
- 8.5 Carbon monoxide, 238
- 8.6 Particulate matter, 240
- 8.7 Lead (Pb), 242
- 8.8 Hydrocarbons and air quality: tropospheric ozone and photochemical smog, 242
- 8.9 Stratospheric ozone chemistry, 245
- 8.10 Sulfur and nitrogen gases and acid deposition, 249
- 8.11 Trace elements in atmospheric deposition: organochlorine pesticides, mercury and other trace elements, 252
  - 8.11.1 Pesticides in air, 252
  - 8.11.2 Hg in air, 253
  - 8.11.3 As, Cd and Ni, 254

Questions, 255

References, 256

## **9 CHEMICAL WEATHERING AND SOILS, 258**

- 9.1 Primary minerals, mineral instability, chemical weathering mechanisms and reactions, soil-forming factors, and products of chemical weathering, 258
  - 9.1.1 Goldich stability sequence, 259
  - 9.1.2 Weathering rates, 260
  - 9.1.3 Chemical weathering, 261
  - 9.1.4 Consequences of chemical weathering: dissolved species and secondary minerals, 264
  - 9.1.5 Geochemical quantification of elemental mobility in soil, 265
  - 9.1.6 Quantifying chemical weathering: CIA, 267
  - 9.1.7 Soil profile, 268
  - 9.1.8 Soil-forming factors, 268
  - 9.1.9 Soil classification – soil orders and geochemical controls, 273
- 9.2 Secondary minerals, controls on their formation, and mineral stability diagrams, 275

9.2.1 Factors controlling soil mineralogy, 275

9.2.2 Mineral stability diagrams, 276

9.3 Soils and the geochemistry of paleoclimate analysis, 281

9.4 Effects of acid deposition on soils and aquatic ecosystems, 282

9.4.1 Increased solubility of Al in acidic soil solution, 283

9.4.2 Displacement of adsorbed nutrient cations, 284

9.4.3 Leaching of base cations enhanced by increased  $\text{NO}_3$  and  $\text{SO}_4$ , 285

9.4.4 Decrease of soil buffering capacity and base saturation, 286

9.4.5 Acid deposition and heavy metals, 287

9.5 Soils and plant nutrients, 287

9.6 Saline and sodic soils, 289

9.7 Toxic metals and metalloids, 290

9.8 Organic soil pollutants and remediation (fuels, insecticides, solvents), 294

Questions, 295

References, 296

## **10 STABLE ISOTOPE GEOCHEMISTRY, 299**

- 10.1 Stable isotopes – mass differences and the concept of fractionation, 299
- 10.2 Delta ( $\delta$ ) notation, 302
- 10.3 Fractionation: vibrational frequencies, temperature dependence, 304
  - 10.3.1 Stable isotopes and chemical bond strength, 305
  - 10.3.2 Temperature-dependent stable-isotope fractionation, 305

10.3.3 Equilibrium and non-equilibrium isotope fractionation, 307

10.4  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , 309

10.4.1 Paleotemperature analysis using oxygen and hydrogen isotopes, 314

10.4.2 Oxygen and hydrogen isotopes as tracers in the hydrologic cycle, 314

10.4.3 Application of oxygen and hydrogen isotopes to paleosol climate records, 316

10.5  $\delta^{15}\text{N}$ , 316

10.6  $\delta^{13}\text{C}$ , 318

10.6.1 Carbon isotope analysis of paleoenvironment, 320

10.6.2 Carbon isotopes in hydrology and chemical weathering, 321

10.7  $\delta^{34}\text{S}$ , 321

10.7.1 Fraction of sulfur isotopes, 322

10.8 Non-traditional stable isotopes, 324

10.8.1  $\delta^{65/63}\text{Cu}$ , 325

10.8.2  $\delta^{56/54}\text{Fe}$ , 326

10.8.3  $\delta^{202/198}\text{Hg}$ , 326

10.8.4  $\delta^{26}\text{Mg}$  and  $\delta^{44/42}\text{Ca}$ , 328

10.8.5  $\delta^{37/35}\text{Cl}$ , 330

10.9 Summary, 330

Questions, 331

References, 331

## **11 RADIOACTIVE AND RADIOGENIC ISOTOPE GEOCHEMISTRY, 335**

11.1 Radioactive decay, 335

11.1.1 Decay mechanisms and products, 336

11.1.2 Half-lives, decay rates and decay constants, 337

11.2 Radionuclides as tracers in environmental geochemistry, 341

11.2.1  $^{206}\text{Pb}/^{207}\text{Pb}$ , 341

11.2.2  $^{87}\text{Sr}/^{86}\text{Sr}$ , 342

11.3 Radionuclides as environmental contaminants, 342

11.3.1 Controls on U, Th and their decay products, 342

11.3.2 Refined uranium ores and associated nuclear wastes, 346

11.3.3 Geological disposal of high-level radioactive wastes, 349

11.4 Geochronology, 350

11.4.1  $^{14}\text{C}$ , cosmogenic radionuclides and earth-surface dating techniques, 350

11.4.2 Common radioactive decay methods of dating sediments and minerals, 359

11.4.3  $^{234}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}$  disequilibrium, 364

Questions, 367

References, 367

## **APPENDIX I CASE STUDY ON THE RELATIONSHIP OF VOLATILE ORGANIC COMPOUNDS (VOCs), MICROBIAL ACTIVITY, REDOX REACTIONS, REMEDIATION AND ARSENIC MOBILITY IN GROUNDWATER, 371**

I.1 Site information, contaminant delineation, 371

I.2 Remediation efforts, 372

I.3 Sources of PCE and As, 374

I.4 Mobilization of arsenic, 374

References, 377

## **APPENDIX II INSTRUMENTAL ANALYSIS, 378**

II.1 Analysis of minerals and crystal chemistry, 378

- II.1.1 Electron microscopy (SEM, TEM and many other acronyms), 378
- II.1.2 X-ray diffraction, 379
- II.1.3 FTIR, 382
- II.1.4 Elements in solution by ICP-AES, ICP-MS, AAS, 384
- II.1.5 XRF, 385
- II.1.6 X-ray absorption spectroscopy (XAS) techniques (EXAFS, XANES), 385

II.1.7 Isotopic analysis: mass spectrometry, 387

II.1.8 Chromatography, 389

References, 389

### **APPENDIX III TABLE OF THERMODYNAMIC DATA OF SELECTED SPECIES AT 1 ATM AND 25 °C, 390**

Index, 394