

This book provides a comprehensive introduction to the field of geochemistry. The book first lays out the 'geochemical toolbox': the basic principles and techniques of modern geochemistry, beginning with a review of thermodynamics and kinetics as they apply to the Earth and its environs. These basic concepts are then applied to understanding processes in aqueous systems and the behavior of trace elements in magmatic systems. Subsequent chapters introduce radiogenic and stable isotope geochemistry and illustrate their application to such diverse topics as determining geologic time, ancient climates, and the diets of prehistoric peoples. The focus then broadens to the formation of the solar system, the Earth, and the elements themselves. Then the composition of the Earth itself becomes the topic, examining the composition of the core, the mantle, and the crust and exploring how this structure originated. A final chapter covers organic chemistry, including the origin of fossil fuels and the carbon cycle's role in controlling Earth's climate, both in the geologic past and the rapidly changing present.

Geochemistry is essential reading for all earth science students, as well as for researchers and applied scientists who require an introduction to the essential theory of geochemistry, and a survey of its applications in the earth and environmental sciences.

William White teaches geochemistry as a Professor of earth and atmospheric sciences at Cornell University. He received a B.A. in geology from the University of California, Berkeley and a PhD in oceanography from the University of Rhode Island. He is a fellow of the Geochemical Society/European Association of Geochemistry and the AGU, and has been named a highly cited author by ISI.



A companion website with additional resources is available at www.wiley.com/go/white/geochemistry



Also available
as an e-book

 **WILEY-BLACKWELL**

www.wiley.com/wiley-blackwell



Contents

About the companion website	viii
Chapter 1: Introduction	1
1.1 Geochemistry	1
1.2 This book	2
1.3 The philosophy of science	4
1.4 Elements, atoms, and chemical bonds: some chemical fundamentals	6
1.5 A brief look at the Earth	15
References and suggestions for further reading	19
Chapter 2: Energy, entropy and fundamental thermodynamic concepts	20
2.1 The thermodynamic perspective	20
2.2 Thermodynamic systems and equilibrium	21
2.3 Equations of state	24
2.4 Temperature, absolute zero, and the zeroth law of thermodynamics	26
2.5 Energy and the first law of thermodynamics	27
2.6 The second law and entropy	30
2.7 Enthalpy	38
2.8 Heat capacity	39
2.9 The third law and absolute entropy	47
2.10 Calculating enthalpy and entropy changes	48
2.11 Free energy	51
2.12 The maxwell relations	58
References and suggestions for further reading	58
Problems	59
Chapter 3: Solutions and thermodynamics of multicomponent systems	61
3.1 Introduction	61
3.2 Phase equilibria	62
3.3 Solutions	67
3.4 Chemical potential	68
3.5 Ideal solutions	71
3.6 Real solutions	73
3.7 Electrolyte solutions	80
3.8 Ideal solutions in crystalline solids and their activities	88
3.9 Equilibrium constants	89
3.10 Practical approach to electrolyte equilibrium	96
3.11 Oxidation and reduction	100
References and suggestions for further reading	110
Problems	111

Chapter 4:	Applications of thermodynamics to the Earth	116
4.1	Introduction	116
4.2	Activities in non-ideal solid solutions	116
4.3	Exsolution phenomena	120
4.4	Thermodynamics and phase diagrams	122
4.5	Geothermometry and geobarometry	128
4.6	Thermodynamic models of magmas	137
4.7	Reprise: thermodynamics of electrolyte solutions	145
	References and suggestions for further reading	154
	Problems	156
Chapter 5:	Kinetics: the pace of things	160
5.1	Introduction	160
5.2	Reaction kinetics	161
5.3	Relationships between kinetics and thermodynamics	172
5.4	Diffusion	179
5.5	Surfaces, interfaces, and interface processes	191
5.6	Kinetics of dissolution and leaching	201
5.7	Diagenesis	207
	References and suggestions for further reading	211
	Problems	213
Chapter 6:	Aquatic chemistry	217
6.1	Introduction	217
6.2	Acid–base reactions	217
6.3	Complexation	231
6.4	Dissolution and precipitation reactions	239
6.5	Clays and their properties	249
6.6	Mineral surfaces and their interaction with solutions	253
	References and suggestions for further reading	265
	Problems	265
Chapter 7:	Trace elements in igneous processes	268
7.1	Introduction	268
7.2	Behavior of the elements	270
7.3	Distribution of trace elements between coexisting phases	281
7.4	Factors governing the value of partition coefficients	283
7.5	Crystal-field effects	294
7.6	Trace element distribution during partial melting	299
7.7	Trace element distribution during crystallization	310
7.8	Summary of trace element variations during melting and crystallization	315
	References and suggestions for further reading	316
	Problems	318
Chapter 8:	Radiogenic isotope geochemistry	321
8.1	Introduction	321
8.2	Physics of the nucleus and the structure of nuclei	322
8.3	Basics of radiogenic isotope geochemistry	330
8.4	Decay systems and their applications	334
8.5	Cosmogenic and fossil isotopes	360
	References and suggestions for further reading	365
	Problems	367
Chapter 9:	Stable isotope geochemistry	371
9.1	Introduction	371
9.2	Theoretical considerations	373

9.3	Isotope geothermometry	384
9.4	Isotopic fractionation in the hydrologic system	387
9.5	Isotopic fractionation in biological systems	388
9.6	Paleoclimatology	396
9.7	Hydrothermal systems and ore deposits	404
9.8	Stable isotopes in the mantle and magmatic systems	409
9.9	Isotopes of boron and lithium	417
	References and suggestions for further reading	424
	Problems	428
Chapter 10:	The big picture: cosmochemistry	430
10.1	Introduction	430
10.2	In the beginning . . . nucleosynthesis	431
10.3	Meteorites: essential clues to the beginning	442
10.4	Time and the isotopic composition of the solar system	456
10.5	Astronomical and theoretical constraints on solar system formation	467
10.6	Building a habitable solar system	478
	References and suggestions for further reading	489
	Problems	492
Chapter 11:	Geochemistry of the solid earth	493
11.1	Introduction	493
11.2	The Earth's mantle	493
11.3	Estimating mantle and bulk earth composition	502
11.4	The Earth's core and its composition	510
11.5	Mantle geochemical reservoirs	516
11.6	The crust	529
	References and suggestions for further reading	557
	Problems	561
Chapter 12:	Organic geochemistry, the carbon cycle, and climate	563
12.1	Introduction	563
12.2	A brief biological background	564
12.3	Organic compounds and their nomenclature	565
12.4	The chemistry of life: important biochemical processes	575
12.5	Organic matter in natural waters and soils	580
12.6	Chemical properties of organic molecules	589
12.7	Sedimentary organic matter and coal and oil formation	599
12.8	Isotope composition of hydrocarbons	614
12.9	The carbon cycle and climate	617
	References and suggestions for further reading	629
	Problems	633
Appendix		635
Index		637