# Contents


| | | |
|---|---|---|
| | **Preface** | **xiii** |
| | **Acknowledgements** | **xiv** |
| Chapter 1 | **Production and fate of organic matter** | **1** |
| 1.1 | **Global carbon cycle** | 1 |
| 1.1.1 | Organic geochemistry and the carbon cycle: an introduction | 1 |
| 1.1.2 | Carbon reservoirs and fluxes between them | 1 |
| | Organisms and carbon cycling | 2 |
| | Accumulation of sedimentary organic matter | 3 |
| | Deviation from the steady state system | 4 |
| | Marine primary production and sedimentation | 4 |
| 1.1.3 | Biochemical and geochemical subcycles | 5 |
| | Organic-rich sediments and primary production | 6 |
| 1.2 | **Photosynthesis and the evolution of life** | 6 |
| 1.2.1 | Atmospheric oxygen, photosynthesis and the first organisms | 6 |
| 1.2.2 | Evolution of marine life | 13 |
| 1.2.3 | Evolution of terrestrial life | 14 |
| 1.2.4 | Regional variations in ecosystems | 15 |
| 1.3 | **Major contributors to sedimentary organic matter** | 16 |
| 1.3.1 | Major present-day contributors | 16 |
| 1.3.2 | The fossil record of major contributors | 17 |
| 1.4 | **Photosynthesis and stable isotopes of carbon** | 18 |
| Chapter 2 | **Chemical composition of biogenic matter** | **22** |
| 2.1 | **Structure of natural products** | 22 |
| 2.1.1 | Introduction | 22 |
| 2.1.2 | Bonding in organic compounds | 23 |
| 2.1.3 | Stereoisomerism | 25 |
| 2.2 | **Carbohydrates** | 28 |
| 2.2.1 | Composition | 28 |
| 2.2.2 | Occurrence and function | 31 |
| 2.3 | **Proteins** | 34 |
| 2.3.1 | Composition | 34 |
| 2.3.2 | Occurrence and function | 37 |
| 2.4 | **Lipids** | 39 |

2.4.1 Glycerides 39
Fats 39
Phospholipids, glycolipids and ether lipids 42
2.4.2 Waxes and related compounds 43
Waxes 43
Cutin and suberin 45
2.4.3 Terpenoids 45
Monoterpenoids 47
Sesquiterpenoids 47
Diterpenoids 47
Triterpenoids 47
Steroids 50
Tetraterpenoids 53
2.4.4 Tetrapyrrole pigments 56
2.5 **Lignin, tannins and related compounds** 58
2.5.1 Lignin 58
2.5.2 Tannins and other hydroxy-aromatic pigments 60
2.6 **Geochemical implications of compositional variation** 61
2.6.1 Compositional variation of organisms 61
2.6.2 Variations throughout geological time 62

Chapter 3 **Conditions for the accumulation of organic-rich sediments** **63**

3.1 **Introduction** 63
3.2 **Factors affecting primary production** 63
3.2.1 Stratification of the water column 65
3.2.2 Light 68
3.2.3 Nutrients 70
Low latitude oceans 71
Middle latitude oceans 72
High latitude oceans 73
Stratified lakes 73
3.2.4 Spatial variation in marine primary production 74
3.2.5 Variation in phytoplankton populations 76
3.3 **Preservation and degradation of organic material** 77
3.3.1 Fate of primary production in the water column 77
3.3.2 Sedimentary fate of organic material 77
Aerobic decomposition 77
Anaerobic decomposition 78
Bacterial communities and their interactions 80
3.3.3 Factors affecting sedimentary preservation of organic matter 82
3.4 **Depositional environments** 84
3.4.1 Lacustrine environments 84
Open lakes 85
Closed lakes 86
3.4.2 Peat swamps and coal formation 87
Okefenokee swamp 88

3.4.3 Marine environments 89
Marine shelf deposits 89
Enclosed and silled basins 90
Production and preservation of organic matter in the Black Sea 91
Cretaceous anoxic events 91

Chapter 4 **Formation of humic material, coal and kerogen** **93**

4.1 **Diagenesis** 93
4.1.1 Introduction 93
4.1.2 Microbial degradation of organic matter during diagenesis 93
4.1.3 Geopolymer formation 94
4.2 **Humic material** 95
4.2.1 Occurrence and classification 95
4.2.2 Composition and structure 95
4.2.3 Formation of humic substances 98
4.3 **Coal** 98
4.3.1 Classification and composition 98
Classification 98
Petrological composition 99
Chemical composition 100
4.3.2 Formation 100
Peatification 101
Biochemical stage of coalification 101
Geochemical stage of coalification 102
Structural changes during coal formation 103
4.4 **Kerogen** 106
4.4.1 Formation 106
Geopolymer formation during diagenesis 106
Biomarkers 109
Sulphur incorporation 110
4.4.2 Kerogen composition 112
4.4.3 Kerogen classification 113
Type I kerogen 113
Type II kerogen 114
Type III kerogen 114
Type IV kerogen 115
Improved kerogen typing 115
4.4.4 Thermal evolution of kerogen 115
Structural changes 115
Changes in chemical composition 116

Chapter 5 **Generation and composition of petroleum** **119**

**5.1 Petroleum generation** 119
5.1.1 Introduction 119

5.1.2 Hydrocarbons from coal 120
5.1.3 Variation in hydrocarbon composition with kerogen maturity 120
5.1.4 Reactions involved in hydrocarbon generation 122
Isotopic fractionation 123
5.2 **Importance of time and temperature in petroleum formation** 124
5.2.1 Effects of time and temperature on hydrocarbon generation 124
Temperature 124
Time 125
5.2.2 Kinetic models of petroleum formation 125
Time–temperature index 125
More complex models 128
5.3 **Migration of hydrocarbons** 129
5.3.1 Primary migration 129
Mechanisms of primary migration 129
Expulsion efficiency 131
5.3.2 Secondary migration 132
5.3.3 Traps and reservoirs 133
5.4 **Petroleum composition** 135
5.4.1 Gross composition of oils 135
5.4.2 Hydrocarbons in petroleum 136
Major hydrocarbons 136
Biomarkers 138
5.4.3 Comparison of crude oil composition with source rock bitumen 140
Migration 140
Water washing 141
De-asphalting 141
Biodegradation 141
Thermal alteration 141
5.5 **Occurrence of fossil fuels** 141
5.5.1 Temporal distribution of fossil fuels 141
5.5.2 Oil reserves 144
Conventional oils 144
Heavy oils 145
Oil shales 145
5.5.3 Coal 146
5.5.4 Gas 146
5.6 **Assessment of petroleum source rocks** 146
5.6.1 Amount and type of organic matter 146
Amount of organic matter 147
Type of organic matter–optical methods 147
Type of organic matter–physico-chemical methods 148
5.6.2 Maturity of organic matter 148
Optical measurements of maturity 148
Pyrolytic measurements of maturity 150
Effect of maturity on identification of organic matter type 150
Chemical measurements of maturity based on bitumen 150
5.6.3 Stable isotopes and correlation of petroleums with source rocks 151

Chapter 6 **Molecular evaluation of Recent sediments** **153**

6.1 **Biomarker distributions inherited from organisms** 153
6.1.1 Introduction 153
6.1.2 General differences between major groups of organisms 154
6.1.3 Factors affecting the lipid composition of organisms 155
6.2 **Examples of source indicators in Recent sediments** 157
6.2.1 Fatty acids 157
Monounsaturated fatty acids 157
Polyunsaturated fatty acids 158
*Iso* and *anteiso* methyl-branched fatty acids 158
Internally branched and cycloalkyl fatty acids 159
Hydroxy fatty acids 159
6.2.2 Sterols 159
6.2.3 Carbohydrates 161
6.2.4 Lignins 162
6.2.5 Carbon isotopes 162
6.3 **Diagenesis at the molecular level** 165
6.3.1 General diagenetic processes 165
Carbohydrates and lignins 165
Biomarkers 166
6.3.2 Lipid diagenesis in the water column 168
6.3.3 Sedimentary diagenesis of lipids 170
Fatty acids 170
Photosynthetic pigments 172
Steroids 175
Terpenoids 179
6.4 **Palaeotemperature measurement** 187
6.4.1 Amino acid epimerisation 187
6.4.2 Degree of unsaturation in long-chain ketones 187

Chapter 7 **Molecular assessment of ancient sediments and petroleum formation** **190**

7.1 **Source indicators** 190
7.1.1 Introduction 190
7.1.2 Hydrocarbons 190
Normal and methyl-branched alkanes 190
Acyclic isoprenoids 191
Cycloalkanes 192
7.1.3 Carbon isotopes 193
7.2 **Indicators of depositional environment** 194
7.2.1 Hypersalinity 194
7.2.2 Redox conditions 195
Phytol diagenesis 195
Nickel and vanadium distributions 197

7.2.3 Recognition of different types of marine and lacustrine environments 198
7.3 **Thermal maturity and molecular transformations** 199
7.3.1 Configurational isomerism 199
Acyclic isoprenoidal alkanes 199
Steranes 199
Triterpanes 200
7.3.2 Aromatisation 201
7.3.3 Enrichment of short-chain hydrocarbons and cracking processes 201
Steroids 201
Porphyrins 201
7.4 **Molecular maturity and source parameters in petroleum exploration** 202
7.4.1 Molecular maturity parameters 202
Light hydrocarbons 202
Carbon preference index 203
Pristane formation index 203
Biomarker transformations 204
Methyl group isomerism in aromatic hydrocarbons 205
7.4.2 Effect of geothermal gradient on molecular maturity parameters 208
7.4.3 Correlation of oils and source rocks 210
7.5 **Biomarker hydrocarbon analysis** 211
7.5.1 Introduction 211
7.5.2 Gas chromatography–mass spectrometry 211
7.5.3 Evaluation of biomarker distributions 213

Chapter 8 **Environmental behaviour of anthropogenic organic compounds** **217**

8.1 **Introduction** 217
8.2 **Human influence on the carbon cycle** 217
8.2.1 Carbon dioxide and the greenhouse effect 217
8.2.2 Effects of other trace gases on global warming 220
Methane 221
Carbon monoxide 223
Dimethyl sulphide 223
8.2.3 Eutrophication 224
8.3 **Halocarbons and ozone depletion** 225
8.4 **Hydrocarbon pollution in aquatic environments** 227
8.4.1 Fossil fuel combustion 227
Polycyclic aromatic hydrocarbons in Recent sediments 227
Polycyclic aromatic hydrocarbons in ancient sediments 228
8.4.2 Oil spills 230
Effects of oil pollution 230
Oil pollution monitoring 231
8.5 **Some xenobiotic organic substances** 232
8.5.1 DDT and related compounds 233

8.5.2 Polychlorinated biphenyls 234
8.6 **Factors affecting the fate of anthropogenic inputs** 237
8.6.1 General considerations 237
8.6.2 Humic substances and pollutants 238

**References** 239
**Further reading** 249
**Index** 253