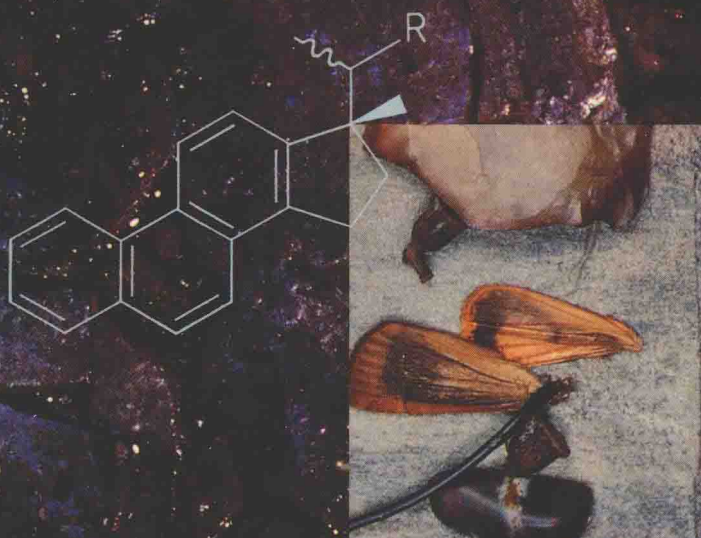
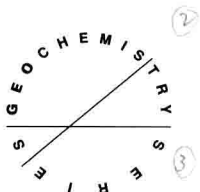


Stephen D Killops
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an introduction to

organic geochemistry





An Introduction to Organic Geochemistry

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Preface

To begin with, a brief statement of what constitutes organic geochemistry is probably called for. It is the study of the transformations undergone by all organic matter from its origin, whether biological or man-made, in the geosphere. The term geosphere is usually interpreted in its widest sense, encompassing the range of possible environments (earth, air, water and sediment). The transformations involved vary from those mediated by biological agents during recycling of the constituents of living organisms to those controlled by temperature and pressure at depth in the crust on the way to long-term preservation of organic matter in sedimentary rock.

Our knowledge of organic geochemistry has expanded so greatly in recent years that a comprehensive text on the subject would fill many books of this size. To a newcomer, the bulk of information and the terminology adopted from a range of disciplines, such as chemistry, geology, ecology, biochemistry, botany and oceanography, can be quite daunting. However, to those who are not readily deterred, the fascination of the subject soon becomes apparent. If only the basics of organic geochemistry could be found readily at hand and not scattered through the textbooks and journals of a number of disciplines! These were our thoughts when we first came to the subject some ten years or so ago and which provided the stimulus for this book when one of us (S.D.K.) came to teach the subject to both undergraduates and postgraduates.

This book is an attempt to present a readily accessible, up-to-date and integrated introduction to organic geochemistry, at a reasonable price. It does not assume any particular specialist knowledge other than some basic chemistry and is intended to serve as a text for both undergraduate and postgraduate courses in which organic geochemistry is an important component. It may also be found a useful companion by experienced scientists from other disciplines who may be moving into the subject for the first time.

Naturally, in a book of this size it is not possible to discuss all aspects of organic geochemistry, and emphasis has been placed on the formation of organic-rich sedimentary deposits. While this approach will be of particular relevance to those interested in petroleum exploration, the important area of environmental geochemistry has also received consideration. In addition, boxes have been used to explain concepts introduced from other disciplines. We hope that this book will stimulate the reader to continue studying organic geochemistry.

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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 petroleum 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
	<i>Iso</i> and <i>anteiso</i> 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

1.1 Global carbon cycle

1.1.1 Organic geochemistry and the carbon cycle: an introduction

Organic geochemistry concerns the fate of all organic compounds in the geosphere as a whole. From chiefly biological origins, organic compounds can be incorporated into sedimentary rocks and preserved for geological periods, but they are ultimately returned to the Earth's surface, either by natural processes or by human action, to participate again in biosynthetic reactions. This cycle involves various biochemical and geochemical transformations, which form a central part of any consideration of organic geochemistry.

The chemistry of organic compounds is based on carbon, the twelfth most abundant element in the Earth's crust. Carbon accounts for only ca. 0.08% of the combined lithosphere, hydrosphere and atmosphere but it is, nevertheless, an extremely important element and its compounds form the basis of all life. Carbon-rich sedimentary deposits are of great importance to humans. They comprise diamond and graphite (the native forms of carbon), calcium and magnesium carbonates (calcite, limestone, dolomite, marble and chalk) and hydrocarbons (gas, oil and coal). The last category is the main consideration of this book. The ability of carbon to form an immense variety of naturally occurring compounds, primarily with the elements hydrogen, oxygen, sulphur and nitrogen, with an equally wide range of properties is unparalleled by other elements.

1.1.2 Carbon reservoirs and fluxes between them

A useful starting point for the study of organic carbon compounds in the biosphere and geosphere is the global carbon cycle. A much simplified summary of this cycle is shown in Fig. 1.1, which gives an idea of the sizes of the various compartments (or **reservoirs**) in which carbon is located, the exchange rates (or **fluxes**) between these reservoirs and the main forms in which carbon exists in each reservoir. The metric tonne (t or 10^3 kg) is a convenient unit for large masses and is used in Fig. 1.1 and throughout the text. All reservoir and flux values in Fig. 1.1 are approximate, as many cannot be measured directly but are inferred from other measurements. It is likely that many of the estimates used will be revised, some by significant amounts, as research progresses. It can be seen that by far the largest reservoir of carbon, accounting for ca. 99.9% of the total, is sedimentary rock, mainly in the form of carbonates. In addition, inputs to and outputs from the various carbon reservoirs are broadly in balance, resulting in what can be considered a steady state system.

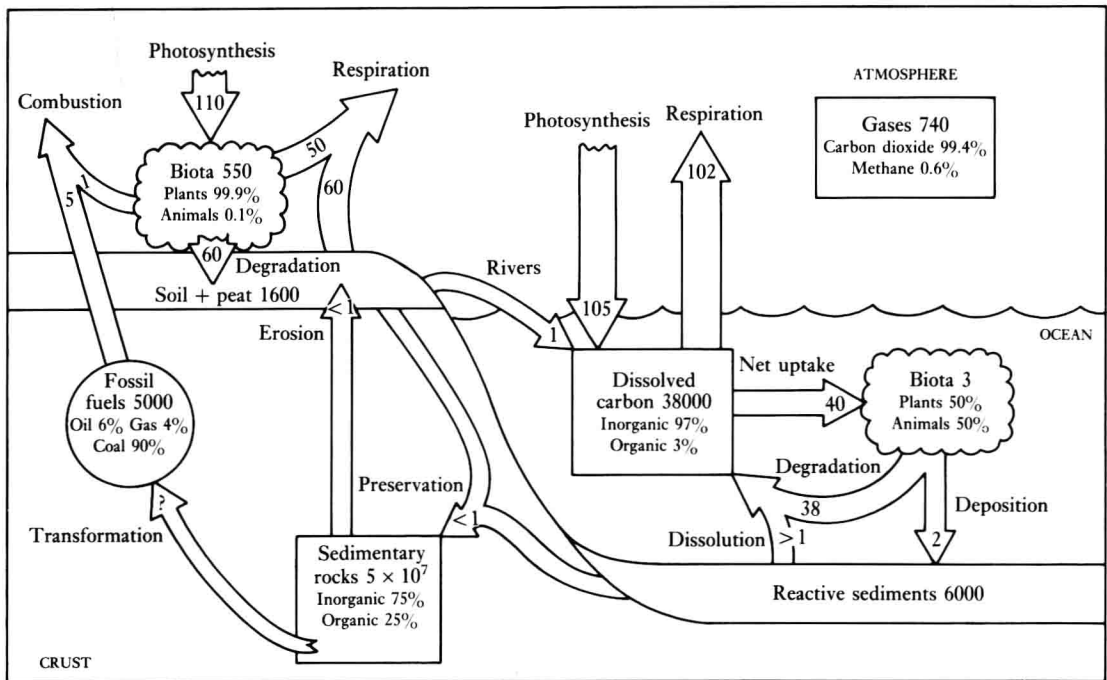


Figure 1.1 Summary of the global carbon cycle, showing sizes of main reservoirs (boxes of various shapes) and annual fluxes (arrows) in units of Gt (10⁹ t or 10¹⁵ g) of carbon. (After several sources, including Bolin et al., 1979, 1983; Kempe, 1979; Mopper and Degens, 1979; De Vooy, 1979; NERC, 1989.)

Organisms and carbon cycling

In the atmosphere carbon exists mainly as carbon dioxide, which is taken up by growing plants during photosynthesis. The amount of solar energy captured by plants during photosynthesis is referred to as **gross primary production** and can be measured by the amount of carbon dioxide that has been fixed. Some of the gross primary production is used to provide the energy needed for the performance of normal biochemical processes, which are collectively termed **respiration**. Respiration can be viewed as the 'burning' of organic compounds to release stored energy and as such is effectively the opposite of photosynthesis, releasing carbon dioxide back into the atmosphere. The part of gross primary production that is not respired, but is available for growth and reproduction, is called **net primary production**.

From Fig. 1.1 it can be seen that the annual net primary production for land plants and marine plants is about the same (ca. 60 and 40 Gt, respectively), although the biomass of terrestrial plants is much greater than that of marine plants. This is an important demonstration of the fact that biomass is not necessarily a guide to productivity. In the ocean 95% of primary production is accounted for by the phytoplankton, which are free-floating, microscopic organisms, mainly unicellular algae. On a global basis macroscopic, multicellular algae (seaweeds) make only a minor contribution to marine primary production. Phytoplankton are short-lived compared with terrestrial plants, especially trees, and do not need to produce supportive structural tissue, which is largely photosynthetically inactive. The larger biomass of terrestrial plants is due to the storage of organic matter as woody material

during greater life spans. Virtually the whole of the net primary production of phytoplankton is directed towards reproduction and growth, but much of this is grazed by small herbivorous animals, called zooplankton. As a consequence of this efficient grazing, phytoplankton biomass is low and the ratio of animal to plant biomass in the oceans is greater than on land.

All organisms rely on solar energy but only plants and some bacteria (e.g. cyanobacteria) are able to make direct use of it in the conversion of carbon dioxide into carbohydrates, the process of photosynthesis. Such organisms are termed **phototrophs**. Some bacteria are able to use chemical energy sources such as ammonia, nitrite and ferrous ions rather than light, and are therefore called **chemotrophs**. Generally, however, the chemosynthesis of organic matter is minor compared with photosynthesis. The phototrophs and chemotrophs are collectively known as **autotrophs** because they can manufacture their organic constituents directly from inorganic sources and do not rely on other organisms for energy supplies. All other organisms gain their energy supplies and organic substrates by feeding, directly or indirectly, upon autotrophs and are termed **heterotrophs**.

Energy is passed from the primary producers to the various heterotrophs along food chains and ultimately reaches the top carnivores. **Herbivores** represent the first link in the **grazing food chain**. Plant tissue that is not consumed by herbivorous animals eventually dies. In a steady state system losses of plant tissue by grazing and death are balanced by net primary production of new tissue. Dead plant matter together with the faecal material of animals and their remains upon death are collectively termed **detritus** and pass to organisms of the **detrital food chain** in soil, water and sediments. Invertebrate animals form one group of detrital-feeding organisms, the **detritivores**, but the most important group is the **decomposers**, which comprises bacteria and fungi.

*Accumulation of
sedimentary
organic matter*

In the marine environment as a whole most detrital organic matter (ca. 95%) is recycled by **pelagic** organisms (i.e. swimming or floating organisms) within the surface waters. The small amount that does reach the sediment is mostly recycled by detrital-feeding **benthic** organisms (which live on top of and within the sediment). Any detrital organic material that survives, under the right conditions (which will be discussed in Chapter 3), may be preserved and incorporated into the sediment and form organic-rich deposits. From Fig. 1.1 it can be seen that the total amount of carbon (organic and inorganic) accumulating in sediments is $<1 \text{ Gt/a}$. It is estimated that the accumulation rate of organic carbon in sediments is ca. 4 Mt/a ($4 \times 10^6 \text{ t/a}$), which suggests that only ca. 0.01% of marine net primary production is preserved annually in sediments (Tissot and Welte, 1984). Even if the accumulation rate has been underestimated it seems probable that annual preservation of organic matter in sediments is $<0.1\%$ of marine net primary production.

Organic matter is virtually completely decomposed and recycled in soils. Preservation of organic matter in terrestrial environments is, therefore, confined mostly to peat formation in moorland bogs and low-lying swamps, but the size of this carbon reservoir (ca. 160 Gt) is not known with any accuracy. While the present annual accumulation rate of peat is low compared with that of organic-rich marine sediments, the presence of large coal deposits in the sedimentary record suggests that peat formation was of much greater importance in the past. Present-day net primary production in freshwater environments is $<1 \text{ Gt/a}$, although carbon-rich deposits are being formed under certain conditions in some lakes. However, lakes

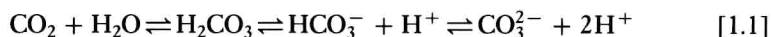
contain only a very small volume of water compared with the oceans and so it is in marine sediments that most of the global preservation of organic carbon is occurring.

*Deviation from
the steady state
system*

As expected for a steady state system, there appears to be a balance between uptake (by photosynthesis) and emission (by respiration) of carbon by terrestrial plants and animals. In contrast, there is an imbalance between uptake and release of carbon dioxide in the marine environment; the oceans seem to be a net sink for carbon dioxide, most of which may be taken up by phytoplankton during photosynthesis. This imbalance is mainly the result of fossil fuel burning and deforestation ('slash and burn'), which are responsible for a net annual surplus input of carbon dioxide to the atmosphere of ca. 3 Gt. The effects of this perturbation to the steady state system will be considered in more detail in Section 8.2.1. Carbon also enters the atmosphere in the form of trace gases such as methane and carbon monoxide. Methane is quantitatively the most important of these trace gases and is mainly produced during the microbial degradation of organic matter in the absence of oxygen. Carbon monoxide is released into the air by natural processes, such as atmospheric oxidation of methane, and by anthropogenic (man-made) processes, such as incomplete combustion of fossil fuels. These trace gases will be considered in more detail in Section 8.2.2.

*Marine primary
production and
sedimentation*

Terrestrial plants take up carbon dioxide directly from the atmosphere in gaseous form. However, aquatic plants utilise carbon dioxide dissolved in water, and it is for this reason that the photosynthesis and respiration flux arrows in Fig. 1.1 do not point directly to the marine biota. Molecules of carbon dioxide are constantly exchanging between the atmosphere and oceans, so that a dynamic equilibrium exists. In solution there are further dynamic equilibrium (reversible) reactions which favour the bicarbonate (HCO_3^-) ion:



These equilibria mean that, at constant temperature, increasing the level of carbon dioxide in the atmosphere causes more to dissolve in the oceans, producing more bicarbonate and carbonate. In seawater most carbon exists in solution, mainly in inorganic forms and particularly bicarbonate. Carbon is chiefly assimilated as bicarbonate and is used in the production of organic tissue as well as, in some cases, the formation of carbonate skeletal material (tests). Carbon is also present in seawater as organic compounds, some being dissolved and some being present as suspended particles. The organic remains of organisms and faecal pellets represent a particulate organic carbon (POC) reservoir of ca. 30 Gt (Mopper and Degens, 1979). Dissolved organic carbon (DOC; ca. 1000 Gt, Fig. 1.1), therefore, accounts for some 97% of the total marine organic carbon. Fluvial particulates contribute little to the open ocean, as they are mainly deposited in estuaries and deltas as a result of slackening currents and flocculation caused by salinity differences.

Carbon-rich sediments may contain both inorganic and organic carbon. Inorganic carbon can be present as **biogenic** or **abiogenic** carbonate (i.e. of biological or non-biological origin, respectively). The former derives from the carbonate tests secreted by some planktonic organisms (e.g. coccolithophores), while the latter is formed by the chemical process of precipitation of carbonate out of seawater solution. Sedimentary organic carbon is mainly in the form of POC that has settled out from the overlying water column. Detritus is, therefore, generally important in the formation of carbon-rich sediments.

After the incorporation of detritus into marine sediments, recycling of carbon can continue in the upper sediment layers, the reactive sediments in Fig. 1.1. Inorganic carbonate and soluble organic compounds produced by decomposition processes can be leached out of these sediments into pore waters, which are able to exchange with water overlying the sediments. With increasing sedimentation this process of exchange ceases and long-term preservation can occur as sediments become consolidated and form sedimentary rocks. The amount of carbon in sedimentary rocks can be calculated from estimates of the total volume of different types of sedimentary material and their average carbon contents (Kempe, 1979). Such an approximation gives the value of ca. 55 Pt (55×10^{15} t) for the sedimentary rock carbon reservoir in Fig. 1.1. The carbon content of the entire Earth's crust has recently been estimated at 90 Pt (NERC, 1989). Of the organic carbon entering sediments ($<0.1\%$ of marine net primary production), much is decomposed, ultimately to CO_2 . However, a proportion is preserved in sedimentary rocks, but the amount of this transformed into fossil fuels on an annual basis is not known with any degree of certainty. The cycle for this organic material is completed by human exploitation of fossil fuels and by the action of natural processes, such as volcanism and the weathering of uplifted and exposed sedimentary rocks.

1.1.3 Biochemical and geochemical subcycles

In this book we are concerned with the organic components of the carbon cycle. It is convenient to consider the organic carbon cycle as comprising two subcycles. The larger (ca. 12 Pt of C, or 12×10^{15} t, calculated from organic content of sedimentary rocks in Fig. 1.1) involves sedimentary rocks and residence times of millions of years, and may be thought of as the **geochemical subcycle**. The smaller (ca. 3 Tt of C, or 3×10^{12} t, calculated from DOC, POC, biota biomass and soil organics in Fig. 1.1) involves biological recycling and residence times of up to a hundred years or so only, and may be thought of as the **biochemical subcycle**. These two subcycles are linked by a small two-way flux. That from biochemical to geochemical subcycle is the rate of incorporation of organic carbon into sedimentary rocks, estimated at presently <1 Gt/a, although it has varied significantly in the past. In a steady state there would be an equal flux in the opposite direction corresponding to erosion of sedimentary rocks. However, human exploitation of fossil fuels has greatly augmented this flux from geochemical to biochemical subcycle.

While the larger, geochemical, subcycle is quantitatively the most important (ca. 99.95% of total organic carbon), all the organic matter in this cycle has originated from the biochemical subcycle (i.e. from plant and animal tissue). This demonstrates that the examination of biological processes in the production and modification of organic matter is as important as considering sedimentary processes in understanding the conditions under which organic-rich sediments are formed. The link between the biochemical and geochemical subcycles is also reflected by the relationship between the quantity of free oxygen in the atmosphere and the amount of reduced carbon compounds preserved in sediments and rocks. This relationship stems from the production of oxygen when carbon dioxide is 'fixed' during photosynthesis, but its removal from the atmosphere when reduced organic compounds (e.g. fossil fuels) are released from the geosphere and are oxidised to carbon dioxide (see Box 1.1).