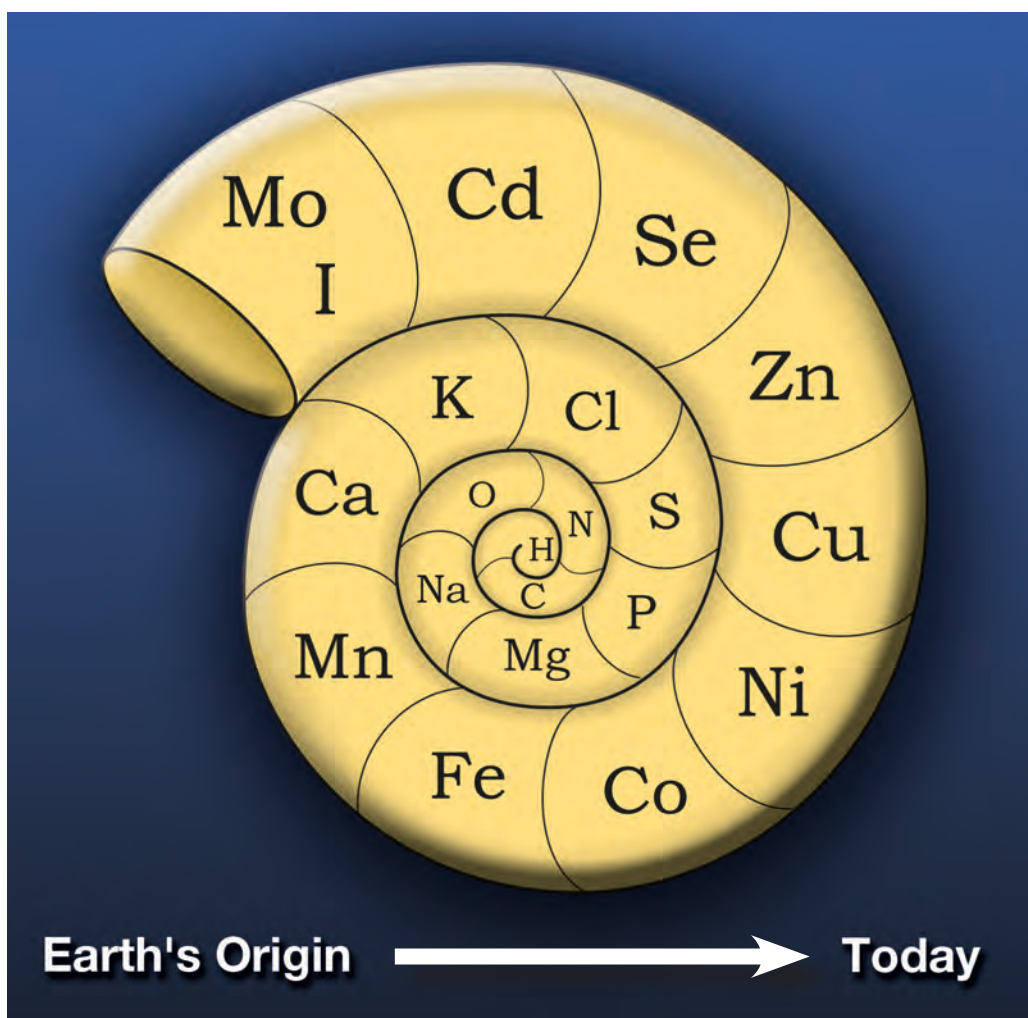


R. J. P. Williams and R. E. M. Rickaby

Evolution's Destiny

Co-evolving Chemistry of the Environment and Life



RSC Publishing

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Preface

This book is written as an addition both to Darwin's work and that of molecular biologists on evolution, so as to include views from the point of view of chemistry rather than just from our knowledge of the biology and genes of organisms. By concentrating on a wide range of chemical elements, not just those in traditional organic compounds, we show that there is a close relationship between the geological or environmental chemical changes from the formation of Earth and those of organisms from the time of their origin. These are considerations that Darwin or other scientists could not have explored until very recent times because sufficient analytical data were not available. They lead us to suggest that there is a combined geo- and biochemical evolution, that of an ecosystem, which has had a systematic chemical development. In this development the arrival of new very similar species is shown to be by random Darwinian competitive selection processes such that a huge variety of species coexist with only minor differences in chemistry and advantages, which is in agreement with previous studies. By way of contrast, we observe that on a large scale, groups of such species have special, different energy and chemical features and functions so that in fair part they support one another. It is more difficult to understand how they evolved and therefore we examine their energy and chemical development in detail. Overall we know that there is a cooperative evolution of a chemical system driven by capture of energy, mainly from the Sun, and its degradation, in which the chemistry of both the environment and organisms are facilitating intermediates. We will suggest that the overall drive of the whole joint system is to optimise the rate of this energy degradation. The living part of the system, the organisms, is under the influence of inevitable inorganic environmental change which moves rapidly to equilibrium conditions, though much of it was forced by the different chemicals added to it by organisms at different times. We are also able to explore some ways in which the organic chemicals of

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organisms evolved. Such evolution was dependent on the inevitably changing environment for all its chemicals and therefore much novel organic chemistry followed a determined path. We recognise that as complexity of the chemistry of organisms increased, the organisms had to become part of a cooperative overall activity and could not remain as isolated species. Prokaryotes and bacteria managed by long-distance exchange between different cells; eukaryotes evolved by incorporating some bacteria – the organelles. The eukaryotes also had increasing numbers of other compartments found in both animals and plants. Later division of essential activities was by direct combination of differentiated cells and by further different forms of symbiosis. Only in the last chapter do we attempt to make a connection between the changing chemistry of organisms with the coded molecules, DNA, of each cell which have to exist to explain reproduction.

This book has to encompass the full spectrum of chemistry, from the extreme of Earth Sciences to those of Biological Sciences. No author can claim to cover all these disciplines to an appropriate depth. The authors of this book apologise for misjudgements of any particular topics and trust that readers will inform them of any errors.

Acknowledgements

We are indebted to the University of Oxford and to the Royal Society for support. We are also grateful to Susie Compton for her help in typing the documents and David Sansom for the illustrations. RR acknowledges financial support from the ERC, grant SP2-GA-2008-200915.

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Glossary

Biological

Anaerobic The condition of the environment and organisms in the absence of oxygen.

Aerobic The condition of the environment and organisms in the presence of oxygen which they utilise.

Micro-aerobic The condition of the environment and organisms in the presence of extremely low levels of oxygen but sufficient to produce some sulfate or ferric ions which assist in prokaryote metabolism.

Prokaryotes The earliest cellular life including both bacteria and Archaea. Earliest date 3.5 Ga. They have a simple rigid membrane enclosing all chemical activities.

Eukaryotes (a) Single cell. These cells evolved at about 2.5 Ga, from prokaryotes? They are large cells with a flexible outer membrane and contain many vesicles including organelles, mitochondria and chloroplasts. They are strictly aerobic.

(b) Multicellular. These organisms are the immediate precursors of the plant, fungal and animal organisms of today. They developed after cellular clusters with an outer containing membrane or 'skin' with many types of differentiated cells or groups of cells (organs) internally. They have an extracellular, but internal to the organisms, connective structure and fluids.

Cytoplasm The main internal solution of all cells.

Periplasm The outermost region of a prokaryote cell between its inner membrane and its outer wall or membrane.

Nucleus The central unit of DNA. It is relatively simple in prokaryotes but much more complex in eukaryotes in a separate compartment.

Vesicle Any membrane-enclosed space with no nucleus.

Plasmids Small units of DNA separate from the nucleus.

Mitochondria see Organelles

Chloroplasts see Organelles

Organelles Eukaryotes capture bacteria and modify them so that they remain internal and partly functional. This may be to reduce complexity in a single

enclosed volume. They are of two kinds: mitochondria, which can obtain energy from oxygen and reduced organic matter, and chloroplasts which obtain energy directly from the Sun. The chloroplasts produce reductive metabolism and as a consequence liberate free oxygen.

Endoplasmic reticulum The large internal membrane enclosed structures which give rise to multiple forms of internal vesicles such as lysosomes for lysing proteins and peroxysomes containing oxidising enzymes.

Differentiated cells Cells of different activity derived from an 'initial' single stem cell of multicellular eukaryotes which carry out different functions although they have the same DNA. They are the original source of organs.

Species and genes The separation of organisms (species), each with different DNA (genes) (see text for details).

Geological

Ocean/hydrothermal vents Fissures of the upper crust, often near divergent plate boundaries or mid-ocean ridges which allow high-temperature reducing liquid circulating through the hot new ocean crust to enter the sea.

Black smokers Typically high-temperature hydrothermal vents with waters emanating at 350 °C. The black smoke is largely FeMn oxyhydroxides which precipitate on cooling of the fluid due to admixing with ambient seawater.

Igneous rock Rock formed from melts and distinguished from sedimentary rock formed from aqueous solutions.

Upper and lower mantle The mantle is the compositionally different layer immediately beneath the crust which passes seismic waves at a higher velocity than the crust. It is separated into two layers, upper and lower mantle, by a seismic discontinuity at ~660 km.

Crust (continental and oceanic) The outer layer of the Earth which is high in silica, more granitic, (continental crust, ~30 km thick) or lower in silica, more basaltic (oceanic crust, ~7 km thick).

Pegmatite A very coarsely crystalline intrusive rock of granitic composition.

Banded iron formation (BIF) Distinctive units of sedimentary rock that are almost always of Precambrian age. A typical BIF consists of repeated, thin layers of iron oxides, either magnetite (Fe₃O₄) or hematite (Fe₂O₃), alternating with bands of iron-poor silicates, shale and chert.

Snowball Earth Periods when there is geological evidence to suggest that glacial conditions extended to equatorial latitudes.

Subduction The process by which one tectonic plate moves under another tectonic plate, sinking as the plates converge.

Cambrian Explosion The rapid (quasi-simultaneous) emergence of multicellular and biomineralised life across multiple phyla at 542 Ma seen in the fossil record.

Mass independent isotopic fractionation Any process that acts to separate isotopes, where the amount of separation does not scale in proportion with the difference in the masses of the isotopes.

Aragonite A metastable calcium carbonate mineral, one of the two common, naturally occurring, crystal forms of CaCO_3 (the other being the mineral calcite). Aragonite has a low magnesium content.

Abbreviations

Ma	Millions of years ago
Ga	Gigayears ago (billions of years ago)
‰	In percentages of units per mil.
BIFs	Banded Iron Formations
REE	rare earth element

About the Authors

Professor R. J. P. Williams F.R.S., Emeritus Napier Royal Society Professor at Oxford and Fellow of Wadham College, Oxford. Professor Williams is often called the Grandfather of Biological Inorganic Chemistry, a subject which he started in 1953. He has published over 700 papers on this and related subjects and he is the coauthor of several related books, including *The Biological Chemistry of the Elements*. He is a medallist of several academic societies and has been awarded Honorary Degrees from Universities in the UK and abroad.

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CHAPTER 1

Outline of the Main Chemical Factors in Evolution

1.1 Introduction to the Chemistry of the Ecosystem

This chapter contains a general introduction to the multidisciplinary subject that includes chemistry, geochemistry, biochemistry and biology of the evolution of and on Earth, *i.e.* both the environment and its organisms. The book does depend heavily on chemistry so we give an outline of the principles of chemistry in this chapter for a reader who is not familiar with it as a discipline. Chemists may wish to skip quickly over Sections 1.2 to 1.6. In the minds of most scientists the evolution of organisms is based solely on organic chemicals, which quantitatively form by far the largest part of all living systems. In the book we wish to explore an additional part of this evolution, which in the first instance seems to be of little relevance to that of organisms. We refer to the early presence and the evolution of the inorganic surface of Earth, *i.e.* the atmospheric gases, the minerals and their solutions, mainly in the sea which, together, have formed the later changing environment for life. Here we consider these two parts of evolution, inorganic and organic, to be interacting in a common ecosystem. We will show that a major feature of life and its evolution, in addition to developing organic chemistry, is a changing availability and adopted essential use of selected inorganic chemical elements from this environment in cells. Many of these chemicals were dissolved from their minerals into solution (Table 1.1), increasingly by weathering, and then were taken into the cells of organisms.¹ (A cell can be looked upon as an enclosed volume of space, in part permeable to particular chemicals.) Eventually these chemicals were returned to the environment, frequently in a transformed state. These elements perform one essential role in cellular

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Table 1.1 Some Minerals from Weathering and Indirect Biological Causes

<i>Mineral</i>	<i>Source</i>
$\text{CaCO}_3(\text{Mg})$	Adsorption of original CO_2 by initial ions from the weathering of silicates
Mg_2SiO_4	Weathering of magnesium oxides
$\text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3$	The products of oxidation of Fe^{2+} seen in Banded Iron Formations
BaSO_4	Due to the oxidation of sulfide

Note. There are many other minerals formed from these two causes in small quantities

catalysis – they are required to activate the small molecules, such as H_2O , H_2 and O_2 , and those in some organic metabolic cellular chemical reactions. The need for them follows from the fact that, although all organic chemicals are thermodynamically unstable relative to stable CO_2 , especially in the presence of the small molecules H_2O and O_2 , they are generally kinetically quite stable at 20 °C. (Virtually all organic chemicals are kinetically unstable at >150 °C, particularly to hydrolysis and oxidation, implying that life has a restricted temperature range, that of liquid water, say from –10° to 150 °C.) At low temperature, 20 °C, they require energy input and catalysed activation in order to bring about synthesis, as well as catalysts for degradation. Therefore both energy and catalysts were required to activate organic chemicals before there could be any coded cellular chemistry, which we call life. The major catalytic inorganic ions are frequently strongly bound and of moderate or slow exchange rate in molecules. They are absolutely required. The essential role of other inorganic elements, which are poor catalysts, lies in their much weaker binding and fast exchange. These properties and the larger available quantities of these elements in the sea make them irreplaceable both in the management of osmotic and electrical balance of cells and in fast transfer of information, *i.e.* in message transmission necessary for balance between the several restricted paths of organic chemical change in cells. Later their fast transfer from outside to inside cells enabled organisms to respond quickly to rapid changes in their environment. The advantage of the exchange of some trace catalytic elements extended to their use in maintaining metabolic homeostasis inside cells. They also acted as controls of genetic expression in transcription factors.

A special chemical interest will be in the controlled biominerals (Table 1.2), produced by, even in, many organisms and giving rise to fossils,^{2–5} as well as those made by their decomposition as deposits on the surface of Earth after death, *e.g.* the White Cliffs of Dover in the south of England and the grains of some deserts, called diatomaceous earth.⁵ All these features of fossil and general biochemistry provide firm evidence of the coupled evolution of life with that of the surface of the Earth. We shall be led to propose that as well as the Darwinian random search amongst species of organisms for those of greatest survival value, associated with the small advantages of certain of them under given slowly changing environmental conditions,[†] there was and is a systematic larger-scale evolution dependent upon the opportunities which the

Table 1.2 The Major Biominerals

<i>Mineral</i>	<i>Variations</i>
SiO ₂	SiO _n (OH) _{2m-n} ($n < 2, m < 2$)?
Ca(Mg)CO ₃	Various forms, many with impurities: calcite, aragonite
Ca ₂ (OH)PO ₄	Apatite with impurities
SrSO ₄	In Acantharia (pure)
BaSO ₄	In a few plants
CaF ₂	In shrimps

Many other biominerals are listed and described in specialist publications⁵

large-scale evolving chemical element environment provided. It is, we believe, this strong and faster environmental development, in a given chemical direction, that guided the way to today's organisms in a systematic, overall much slower, chemical evolution.⁶ However, the increasing complexity ruled out the possibility that they could manage it all, especially the novel oxidation chemistry and the original reductive chemistry in one compartment. As stress increased from oxidation it became necessary to produce different types of prokaryotes, bacteria, and in succession multicompartment then also multicellular organisms and mutually dependent organisms (symbiosis). Many of their evolving changes are seen in the inorganic chemical content of different organisms.

A particular problem we wish to tackle then is the changing role of the inorganic elements both in solution and in minerals in the evolution of the ecosystem. We shall observe that it is the waste by-products of the cellular organic chemistry, particularly oxygen, which initiated relatively quickly the major changes in environmental inorganic chemistry. The timing of the changes depended on their redox potential. We shall then show that it is the back-reaction of these changes which in turn affected the evolution of organisms. The two are in an interactive feedback system. In summary we have to examine the evolution of environmental and cellular inorganic with that of cellular organic/inorganic chemistry. In doing so it is extremely helpful to follow initially the geological (inorganic) chemical record of all the minerals, especially that of sediments and their impurities. The minerals include fossils, the most clear-cut evidence of organism evolution available (see Chapter 3).⁴ To do so we divide the surface minerals of Earth into four classes.² (i) Minerals formed without any intervention of solution or biological activity, for example on the solidification of melts, magma. (ii) Mineral sediments, formed later by weathering of rocks (see Table 1.1). (iii) Minerals which have arisen from chemical transformations

[†] The phrase often used in this context is 'survival of the fittest', which implies competition. All we can observe is the organisms that survived at a given time and it is difficult to know the meaning of fitness, especially as the environment at a given time is unknown. The problem is illustrated by the history of the dinosaurs. We shall observe later that as organisms evolved they became mutually dependent. This indicates that it is a total system that evolves, including the environment and organisms.

of elements in the sea and where it is release of chemicals from organisms, *e.g.* oxygen, which have caused their transformation such as oxidation of iron, giving Fe_3O_4 and Fe_2O_3 precipitates,⁵ and oxidation of sulfide to precipitated sulfur or released soluble sulfate and to release trace elements (see Table 1.1). With those chemicals from weathering, they gave the trace elements typical of the sea at a given time. (iv) Biominerals where the mineral remains attached to the cell surface or which grow internally in the organisms and are easily seen in fossils (see Table 1.2).³ Confusing the issue somewhat is the production of some of the same minerals by more than one of these routes. The history of all these geological deposits has been dated in geological periods (Table 1.3), *i.e.* when a variety of surface rocks and sediments formed (see Sections 2.5 to 2.11). We shall also use this geological table with reference to the timetable of evolution of organisms and related fossils with associated chemistry in the ecosystem. As we have already noted, making the main physical–chemical connection between these minerals and living organisms is the solubility of ions from them, especially in the sea. The limiting possible changes of the inorganic content of the sea at any time arose directly from hydrothermal interaction with basalt, from weathering, or indirectly from chemical reactions of the minerals with chemicals released by cells, and from the death of organisms. We turn to which elements are of importance in the environment and of great influence upon the nature of life and its evolution.

1.1.1 The Involvement of the Elements in Evolution

Not all the elements of the Periodic Table (Figure 1.1) are involved in evolution to any marked degree, certainly to 1900 AD. In addition to hydrogen, carbon and oxygen we shall be concerned with the major ions of

Table 1.3 Geological Periods

<i>Period</i>	<i>Date $\times 10^6$ (yrs) ago</i>	
Archaean Eon	4,500 – 2,500	Earth Forms Prokaryotes
Proterozoic Eon	2,500 – 1,000	First Single-cell Eukaryotes Slow Oxygen Rise
Ediacaran	1,000 – 542	First Multi-cell Eukaryotes Next Oxygen Rise
Cambrian	542 – 488	Biominerals Explosion of Species
Ordovician	488 – 443	Vertebrates First Land Plants
Silurian	443 – 415	
Devonian	415 – 358	
Carboniferous	358 – 300	Coal Formation
Permian	300 – 252	First Extinction
Triassic	252 – 200	
Jurassic	200 – 150	Earliest Birds
Cretaceous	150 – 70	Seeds of Plants
Paleogene	70 – 25	
Neogene	25 →	Homo Sapiens

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
(H)																	He
Li	Be											B	(C)	(N)	(O)	F	Ne
(Na)	(Mg)											Al	Si	(P)	(S)	(Cl)	Ar
(K)	(Ca)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

○ Bulk biological elements □ Trace elements believed to be essential for bacteria, plants or animals ▤ Possibly essential trace elements for some species

Figure 1.1 The Periodic Table indicating the elements of value in organisms.

sodium, potassium, calcium and magnesium, with the anions carbonate, silicate, sulfide (later sulfate) and phosphate in the sea, all of which are also in organisms in considerable amounts. Of these ions, carbonate and sulfide/sulfate showed the greatest changes in concentration later in time. However biological activity is also generally catalysed and controlled by small amounts of ions of several other elements from the sea such as iron, manganese, cobalt, nickel, copper, zinc, molybdenum and selenium and a few others, in particular organisms, all of which have their geological sources largely in mineral oxides (silicates) and sulfides.¹ The availability of some of these ions, found in many biological catalysts, without which there would be no life, changed with time, as seen in sediments. We know that life today depends on some 20 elements which differ, qualitatively and quantitatively, from those which were required initially, and that they all have aqueous solutions as their biological sources, which are for the most part connected to abiotic minerals. Note that very few other elements, if any, have ever been very available in the sea. But why were so many elements needed both in catalysis and in controls of cellular activity?

As we have already stressed there are two spatial parts of chemical activity of early cells which are of particularly different concern, the zone of the internal metabolism and biopolymers and that of the external surfaces, both of which have to be synthesised with the aid of different metal ions. As we shall show, from the beginning of life the use of internal specific powerful catalysts was required in order to activate in particular oxidation/reduction and hydrolytic reactions of rather inert chemicals, *e.g.* H_2 , CH_4 and peptide molecules inside cells, while less powerful catalysts were needed for those reactions which occur relatively easily, *e.g.* hydrolysis of phosphates, inside and outside cells. The different concentrations of ions inside and outside cells

then allowed different metal ions, mostly combined with proteins, to both catalyse and control differentially parts of both internal and external metabolism. The requirement for powerful catalysts of both acid/base and redox reactions inside cells is met by the use of some of the above transition metal ions (Fe, Cu, Zn), as they are of high electron affinity and several can change valence state readily (see Figure 1.6). Moreover several can interact with inert small molecules, such as O_2 , in a specific, idiosyncratic way, so that we observe specific uses for them. The outside surfaces of cells are of molecules which, later in time, say approaching 0.54 Ga, are often selectively changed differently from those inside, again with the aid of strongly but differently active metal ions. They and/or more weakly active metal ions also stabilised these surface molecules. The weaker catalysis often, of acid/base reactions, was more generally executed by non-transition metal ions of lower electron affinity, for example Mg^{2+} and Ca^{2+} , both inside and outside cells. Lastly, bulk osmotic and electrical balance rested with bare ions of no catalytic activity (Na^+ , K^+ and Cl^-), which are in maintained gradients across boundary membranes. To preserve selective action, therefore, cells came to use a considerable variety of metal ions (see Figure 1.1), many of which changed in availability and use with time. Much of this inorganic/organic chemistry is retained in today's cells, but its beginnings are obscure.

Very little if any of the selective catalytic activity of the metal ions was or is due to the bare ions but it arose from active sites, themselves selected, in proteins, enzymes, so that the inorganic chemistry has to be considered with the synthesis of binding proteins as well as with the reactions of organic molecules in cells. One illustrative telling example of the development of external catalysed cell surface reactions, giving rise to biominerals common to later organisms, will be seen to be particularly intriguing during later evolution, because the earliest living cells did not mineralise. The earliest cells left little dependable fossil record, basically only imprints. We shall take it that biomineralisation required particular organic molecules for nucleation, growth and final form.⁵ They arose, relatively suddenly, at a particular time of cellular and environmental chemical change. Biomineralisation is then a signature of the evolution not just of organisms but of particular organic chemistry catalysed by special metal ions, with selected binding of other metal ions and of the oxidising strength at particular times. We shall ask what happened to the environment exactly when these special metal ions and biological mineralisation arose.

We shall also need to describe the historical development of message systems used to create and maintain control of organisation in space and in time, because at all stages of evolution both internal and external cellular activities were and are controlled by messengers. Some of these messengers are free inorganic ions (Fe^{2+} , Mg^{2+} , Ca^{2+} , Na^+ and K^+), but many are organic molecules often requiring catalysis for their synthesis. Now synthesis of the mainly metalloenzyme catalysts is under instruction from genes, coded information, controlled by other messengers. We can of course use knowledge of the evolution of genetic molecules (DNA and RNA), and their expression as proteins, to help examine

all selective internal changes of organic and inorganic cellular components with time. Some of the controlling free metal ion messengers interact with proteins bound to DNA, so-called transcription factors. However genetic information is poor before 0.54 Ga and it is in the period 3.5 to 0.5 Ga when the knowledge of inorganic element changes both in the environment and in cells is most reliable in providing evolutionary markers.

All cellular activity also depends on energy sources, which undoubtedly changed with time too. Both sources of materials (elements) and energy for very early living systems and their changes are probably directly or indirectly dependent upon the mineral environment and its changes from the earliest times. We shall then describe environmental evolution first from its very inorganic beginnings (Chapter 2). We shall try to keep these observed geochemical changes separate from changes in living systems as far as possible, so as to simplify understanding, but during extensive analysis of each separately we will have to bring them together to examine the whole ecosystem from very early times. To appreciate chemical evolution, therefore, we shall have to follow the analytical, chemical content of the inorganic environment with an examination of the later changing organic chemical content of organisms and its energy capture, including the genome, the proteome, the metabolome, and the metallome.^{1,6} Later all energy was from the Sun.

Because our concern is with the environment and organism chemistry and the chemicals which go between them, we need to describe the factors that are important for maintaining the states of both the inorganic and organic chemicals. The constraints on inorganic chemistry are frequently equilibria, thermodynamic relationships which are quantitatively well-defined by constants, solubility products, complex binding constants and redox potentials (see Sections 1.3 to 1.5). The constraints on organic chemistry are quite differently, overwhelmingly, kinetics, rates of reaction, controlled by energy barriers (Section 1.6). Hence many organic chemicals have to be constantly reproduced as they decay. They are energised molecules and react very slowly. They require catalysts and extra energy to change because they are in trapped forms behind energy barriers. We describe next the limiting factors in inorganic chemistry, which give us markers of evolution from geochemistry or studies of the environment and its evolution. These limitations then allow us to make a strong connection to the manner in which organic chemistry and hence organisms could evolve.

Before we begin this analysis of the chemical evolution of an ecosystem we must pay homage to the insight and well-developed theory of life's evolution due to Darwin.⁷ Darwin considered that organisms evolved in an ever-branching tree (Figure 1.2a).⁸ The modern tree (Figure 1.2b) has become generally accepted as being based on survival of the fittest organisms by chance exploration and exploitation of the environment as it changed.⁹ The tree is one of increasing diversity of biological form but must also be in each particular branch, one of increasing chemical complexity. Darwin and more recent biologists describe all this evolution in terms of species, where a species is historically connected by inherited characteristics and today by genes. Their

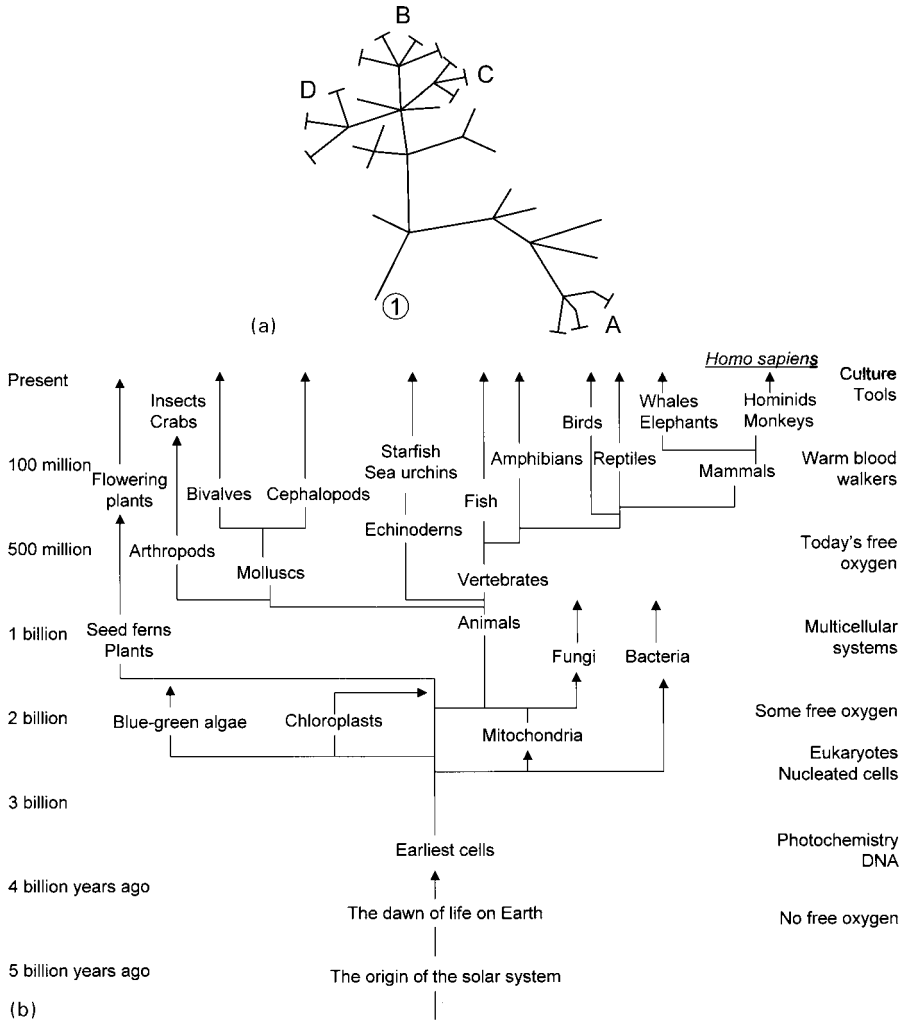


Figure 1.2 (a) Darwin's original musings on a tree of development. (b) A descriptive drawing of the modern "tree" of evolution with an outline of possible dates and of a roughly dated series of events.

discussion has been aided by the observed fossils which could be dated and we will show in Chapter 3 that this study has been greatly extended recently. Now Darwin had virtually no knowledge of the way in which organism or environmental chemistry changed. Indeed in his time there was little knowledge of chemistry. Thus by studying the chemistry of the environment and/or of organisms we can check the idea of random evolution and of an evolutionary tree while examining if it and competitive fitness are correct even in principle.* (The idea of the tree is not an absolute requirement of natural selection.) One very important point Darwin could not have known is that the

environment changes which interact with life were systematic, as we will show, and he regarded all evolution to be without system. Survival of the fittest must be defined against the context of the environment, which we agree is changing systematically. When we examine the standing of evolution in the light of our knowledge of chemistry today, we shall class considerable differences between organisms not in terms of species but as one of chemical element differences in large groups of species, chemotypes.⁶ Chemotypes, we will say, only arose as a consequence of systematic environmental changes, strongly implying that the dependent chemical evolution of groups of organisms has itself to be systematic, contrary to common belief. A chemotype will include many related species of organisms – genotypes. (Here we must note that a gene is related by molecular biologists to a particular stretch of DNA which is inherited and it is often assumed that therefore a species, called man for example, is completely described in its inherited characteristics by its DNA, for man the human chromosomes. In fact the chromosomes are only viable in any organism, man, with many other inherited chemical factors and even symbiotic organisms subsequent to fertilisation of a species cell. We return to the problem in Chapter 4.)

In passing it is sometimes asked if life could have arisen elsewhere. There are two separate issues. We do not have any clear idea how the great complexity of life on Earth arose. Even the very first forms of life we postulate are very complex, as we have indicated above by reference to general organism chemistry, organic and inorganic. It seems to have arisen once on Earth. Thus we do not know how to estimate the probability of it being found on another planet. Secondly we have no certain knowledge of the environmental requirements for life. What was the environment of Earth 3.5 Ga ago? We do know something of the atmosphere, rocks and sea, including the likely temperature and pressure, but we do not know if they are uniquely suitable for engendering life. Table 1.4 gives the composition of Earth in comparison with that of two other planets. There is no possibility of our kind of life on these planets. Mars is or was a better prospect, but possibly only for very primitive life. The idea that we can detect life resembling life on Earth by analyses of elements in objects, in the residues of meteorites, or on the surfaces of planets may well be misleading when we appreciate the demands of the life which have existed or do now exist on Earth. We will see that life has always required close to 20 elements in selected amounts.

In concluding this introduction we stress that our discussion of evolution is based on systematic chemistry and is quite different from other descriptions. We have indicated that the chemistry can be examined not just descriptively

* The phrase often used in this context is 'survival of the fittest', which implies competition. All we can observe is the organisms that survived at a given time and it is difficult to know the meaning of fitness, especially as the environment at a given time is unknown. The problem is illustrated by the history of the dinosaurs. We shall observe later that as organisms evolved they became mutually dependent. This indicates that it is a total system that evolves, including the environment and organisms.

Table 1.4 Composition of Earth, Venus and Mercury

	<i>Earth</i>	<i>Venus</i>	<i>Mercury</i>
H ppm	33	35	0.4
C ppm	446	468	5.1
N ppm	4.1	4.3	0.05
O %	30.1	30.9	14.4
Mg %	13.9	14.5	6.5
Al %	1.4	1.4	1.1
Si %	15.1	15.4	7.0
S %	2.9	1.6	0.2
Fe %	32.0	31.1	64.4
Ni %	1.8	1.7	3.9
Ca %	1.5	1.6	1.2

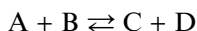
Note Mars is similar to Earth but has a smaller atmosphere like Venus. The outer large planets Jupiter, Saturn, Uranus and Neptune are gaseous. From J.W. Morgan and E. Anders Proc. Natl. Acad. Sci. USA, **77**, 1980, 6973–6977.

but within its systematic character by a quantitative approach. By systematic we imply that the chemical changes are in large part predictable, while previous analyses of evolutionary change have been described by the phrase ‘random selection’. The distinction comes about through the connection between organism and inorganic chemistry rather than through gene changes. The reactions of inorganic compounds are often fast so that they proceed to the most stable condition, quantitative equilibrium. By contrast organic compounds react very slowly because they are unstable but trapped in long lifetime energised states. Hence we consider first the principles of changes of much of inorganic equilibrium chemistry separately from any approach to organic chemistry. Because the organic chemistry is linked to the inorganic chemistry it follows that any changes in organic chemistry will be led by the fast inorganic changes, especially those producing catalysts of organic reactions.

(Those readers familiar with the general principles of equilibria and kinetics may prefer to go immediately to Section 1.7 or to the last section of this chapter (Section 1.10), which is a summary of the main points of concern in this book.)

1.2 Equilibrium and Steady State Conditions

If the rates of transformation of reactants to products and those of the reverse reaction are fast enough in a given solution then the system does not store energy in $C + D$ and is said to be at equilibrium, which we write:



The position of balance, equilibrium, is temperature dependent. It cannot be alive or evolve: it is dead. The main equilibria that will concern us are the solubility products of compounds, complex ion stability constants, and the

standard oxidation/reduction (redox) potentials of elements and compounds in a solution.¹⁰ All the cases of interest are of inorganic compounds, complexes or ions. All the solution-binding equilibria are set up relatively quickly between inorganic ions and with small organic molecules, but as we have explained, organic molecules are not in equilibria with the most stable state of their simple sources, for example H_2 , CO_2 , N_2 , nor with regard to reaction with H_2O or O_2 . Not all the solids of Earth are in equilibrium with their ions either. These sources are only 'stable' in a kinetic description, meaning that they have considerable but limited time of existence. In particular, apart from the large non-equilibrium temperature change from the very centre of Earth to the surface, the rapid original cooling on Earth's formation has left the surface in part in a non-equilibrium energised chemical condition. There are, however, later sediments which we may suppose came to be close to equilibrium with concentrations of components in the sea, which are governed by solubility products, complex ion and redox reaction constants. We shall have to acknowledge that there are exceptions to these generalisations. We outline the nature of the three types of equilibria: solid/solution (solubility products), complex ion formation (stability constants) and reduction/oxidation (standard redox potentials) in the next sections. The concentrations of free individual ions are then mutually dependent on the concentration of partners in these reactions and the redox conditions in the solution.

One general difficulty with both biological and geological systems is that all the material in them is in flow. The flows in biological liquids are not all fast, so that rapid exchanges can reach equilibrium (Table 1.5). Fortunately this is true for many inorganic ionic reactions and reactions of small molecules in solution with one another and with surfaces so that we can apply equilibrium considerations to them, for example incorporation of trace elements in sediments. The flow of other geological systems extends from extremely slow diffusion and movement of such bodies as tectonic plates to the faster motion of materials from volcanic activity and of the mixing of layers of the sea. Again we can select the agents we wish to discuss in these bodies so that we know which have motions fast enough to come to equilibrium locally. Other products are entirely irreversible, *e.g.* initial formation of magma from volcanoes. In many cases in both types of system the flows are strongly, constantly energised, but mixing is fast when the conditions, which are open to analysis though with some difficulty, go towards a steady state, not an equilibrium condition. A biological

Table 1.5 Simplified Classification of Reaction Rates of Bonds

<i>Rate</i>	<i>Chemical Species</i>
Very slow	$\text{C} - \text{H}$, $\text{C} - \text{C}$, $\text{C} - \text{N}$, $\text{C} - \text{O}$, $\text{C} - \text{Halide}$, $\text{S} = \text{O}$
Slow	PO_4R^{2-} , $-\text{CO}_2\text{R}$, $\text{S} - \text{R}$,
Intermediate	Some complex ions <i>e.g.</i> of Cr^{3+} and Co^{3+} , $\text{Mn} = \text{O}$, $\text{Mo} = \text{O}$
Fast	Mg^{2+} , Ni^{2+}
Very fast	Na^+ , K^+ , Cl^- , Ca^{2+} , Zn^{2+} , H^+