15 Coupled Evolution of Earth's Atmosphere and Biosphere

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Summary. Earth's climate has remained conducive to life for more than 3.5 billion years, probably because of higher concentrations of CO_2 and CH_4 greenhouse gases in the past that compensated for a much lower solar flux. Both CO_2 and CH_4 are involved in biogeochemical negative feedback loops that help to stabilize climate. The most significant event in Earth's atmospheric history was an increase in atmospheric O_2. The energetic advantage of aerobic metabolism facilitated larger levels of anabolism (the conversion of simple molecules to complex molecules), which gave rise to multicellular life, anatomical differentiation, and diverse biological complexity. The need for abundant O_2 to facilitate complex life on any planet is probably universal given the thermodynamic uniqueness of oxygen in the periodic table. Earth's atmosphere has evolved to a state that is chemically and physically distinctive compared to the atmospheres on the other planets. Chemically, Earth's atmosphere is continuously maintained at a low entropy state by the biosphere. Physically, Earth is the sunniest planet in terms of energy flux on its surface, while the atmosphere has the most unpredictable weather systems and, paradoxically, the slowest atmospheric jets of any planet with an atmosphere.

15.1 Introduction

The Earth – replete with oceans, forests, and animals – differs vastly from any other planet in the Solar System. However, this cannot have always been so and the question of how the complex world around us developed from lifeless beginnings provides a great interdisciplinary challenge. The geochemical record of ancient rocks and the chemical influence of the modern biosphere tell us that the evolution of life has effected major changes in the chemistry of the atmosphere and oceans. Essentially, the cycling of all elements of use to biology has been partially co-opted by the biosphere. The evolution of oxygenic photosynthesis and its effect on the cycling of elements arguably wrought the biggest change of all. Consequently, the history of atmospheric oxygen provides the environmental framework for discussing the evolution of biological complexity. Without free molecular oxygen, energetic limitations would have precluded life from ever becoming complex. On the other hand, the development of an oxygen-rich atmosphere was perhaps inevitable once bacteria evolved the capability to split water by oxygenic photosynthesis. Coupled with physical process of hydrogen escape to space from the atmo-

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sphere, the Earth's atmosphere was destined to become more oxidized at some point. Once oxygen exceeded a critical threshold, animal life and multicellular plants were the products of opportunistic evolution. Thus, understanding the details of the history of atmospheric oxygen is a key part of the puzzle in understanding how Earth has evolved to be the Solar System's chemical anomaly and how life on Earth evolved to states of lower entropy.

15.2 The Earliest Earth: Its Atmosphere and Biosphere

15.2.1 What Was the Composition of the Prebiotic Atmosphere?

An important question concerning the interaction of the earliest biosphere with the atmosphere is the extent to which the early atmosphere provided a mixture of chemically reducing and oxidized gases of potential metabolic use. Today, the consensus view is that before life appeared, the atmosphere was likely to have been "weakly reducing", composed primarily of N_2, CO_2 and water, with relatively small quantities of H_2, CO, and CH_4, and negligible O_2 (Walker 1977; Kasting and Brown 1998). N_2 was probably similar to present levels, having outgassed early (Fanale 1971). CO_2 may have been present at higher levels (although see Zahnle and Sleep (2000) for an alternative view). Laboratory experiments that produced organic molecules, such as amino acids, in CH_4-NH_3-H_2 atmospheres, had led to suggestions that the early atmosphere was highly reducing to explain how life originated (e.g., Miller 1955). This view has now been largely abandoned, in part, because Rubey (1955) introduced the notion that the atmosphere derived from gases emanating from the solid Earth. Rubey's belief that gradual degassing had led to a slowly increasing atmospheric mass has been replaced by a view of early, rapid degassing (Fanale 1971), but his insight about the redox state of gases entering the atmosphere still holds. Rubey noted that volatiles introduced to the atmosphere from modern degassing are only weakly reducing. Oxidized species such as H_2O, CO_2, and N_2 dominate over the reduced forms, H_2, CO or CH_4, and NH_3. The reduced to oxidized gas ratio (H_2/H_2O, CO_2/CO, etc.) in volcanic gases depends on the degree of oxidation in the upper mantle, the source region for such gases (Holland 1984). Geochemical evidence suggests that much of the mantle's oxidation was completed early, before 3.9 Ga (Canil 1997, 1999, 2002; Delano 2001), possibly during core formation before 4.4 Ga. Hence degassed volatiles have been weakly reducing for most of Earth history and the steady-state prebiotic atmosphere should have reflected this abiotic redox balance.

15.2.2 When Did Earth Acquire a Biosphere?

No one knows exactly when life originated but constraints can be deduced from the geological record and the expected physical environment of the early

Earth. Large impacts that pummeled the early Earth cannot be ignored. In particular, impact objects with size > 440 km would have vaporized all the oceans, sterilizing the planet. Calculations of the occurrence of the last sterilizing impact put a bound on the timing of the origin of the last common ancestor to no earlier than $\sim$4.3–3.8 Ga (Sleep et al. 1989). Geology can tell us when the earliest life is observed. Carbon globules from > 3.7 Ga marine metasedimentary rocks in west Greenland are enriched in ^{12}C by an amount consistent with biological fractionation (Rosing 1999). Reports of older, 3.8–3.9 Ga carbon isotope indicators of life (Mojzsis et al. 1996) are now doubted (Fedo and Whitehouse 2002; van Zuilen et al. 2002). While 3.5 Ga "microfossils" (Schopf 1993) are disputed (Brasier et al. 2002), 3.23–3.47 Ga spherical, carbonaceous microfossils from S. Africa are plausibly biogenic because some are in the process of binary division like cells (Knoll and Barghoorn 1977). Thread-like microfossils also occur in 3.2 Ga deep-sea volcanic rocks (Rasmussen 2000). That microbial life was globally present in the Archean Eon (before 2.5 Ga) can also be inferred from geochemistry. Marine carbonates back to 3.5 Ga are depleted in ^{12}C by an amount similar to modern marine limestone, suggesting that a global biosphere extracted the ^{12}C complement into organic matter (Schidlowski 1988). Indeed, the average organic carbon content of Archean marine shales (fine-grained sedimentary rocks) is $\sim$ 0.5 wt.% , essentially no different from that in recent geological eras. All of this suggests that a global microbial biosphere was present by 3.5 Ga (Nisbet and Sleep 2001).

15.2.3 What Effect Did Primitive Life Have on the Early Atmosphere?

Even the most primitive biosphere would have affected atmospheric composition, shifting it to a greater state of chemical disequilibrium. Today's microbial biosphere affects the cycling of every major element of importance to biology (C, N, O, P, S and so on) and early microbial life no doubt behaved similarly. Life modulates the cycle of carbon, the second most abundant volatile after water, by removing carbon from the atmosphere to synthesize organic matter. Life also modulates the cycle of Earth's third most abundant volatile, nitrogen, by extracting it from the air to make ammonium ions, and then recycling it back to the air. In fact, when early metabolisms evolved they must have particularly affected atmospheric H_2, CO_2, and N_2, because H_2 is food, CO_2 provides a carbon source, and nitrogen is essential for the peptide bond that holds organisms together.

Life would have caused atmospheric H_2 levels to drop (Fig. 15.1), with hydrogen atoms returning to the atmosphere in the form of less edible methane. Methanogens derive energy from hydrogen and carbon dioxide that would have co-existed in the prebiotic atmosphere derived from volatiles continuously degassed from the solid Earth:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{15.1}$$

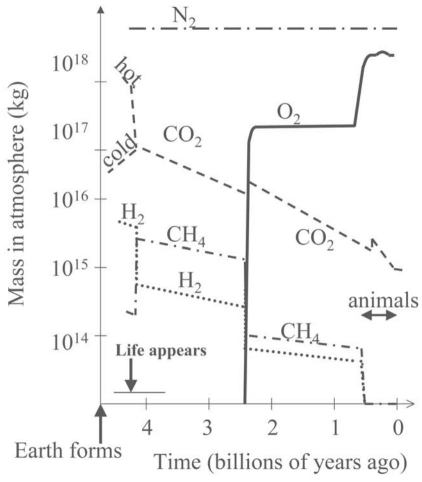

Fig. 15.1. A rough schematic history of the Earth's atmospheric composition. The bifurcation in possible early CO_2 levels reflects the fact that some make the case for a cold, icy start to the early Earth (Sleep and Zahnle 2001), while others argue for a hot beginning (see Schwartzman and Lineweaver, this volume)

The free energy is used by methanogens to synthesize cell material from inorganic nutrients. Assuming that methanogens were thermodynamically limited, $\geq$ 90% of the H_2 would have been converted to CH_4 (Kasting et al. 2001), consistent with laboratory experiments (Kral et al. 1998). Consequently, H_2 levels would have dropped from a prebiotic mixing ratio of 10^{-3} to about $\sim 10^{-4}$ once methanogenesis evolved. CO_2 levels would have also decreased because CH_4 is a powerful greenhouse gas, which would have led to increased warming and loss of CO_2 via temperature-dependent weathering.

Life must have also affected the nitrogen cycle. Nitrogen is often a limiting nutrient because few microorganisms can metabolize nitrogen unless it is fixed from the atmosphere and turned into a soluble form. The first organisms must have relied upon abiotic sources of soluble nitrogen. In the anoxic prebiotic atmosphere, N_2 would have been oxidized with CO_2 by lightning:

$$N_2 + 2CO_2 \rightarrow 2NO + 2CO \qquad (15.2)$$

NO dissolves to produce ${NO_3}^-$ and ${NO_2}^-$ as end products (Mancinelli and McKay, 1988), providing a modest flux of fixed nitrogen (Navarro-Gonzales et al. 2001). Ammonium could have also been produced from HCN hydrolysis because HCN is synthesized in atmospheres containing trace levels of CH_4. In any case, once anaerobes developed nitrogen fixation, ${NH_4}^+$ would likely have become the dominant combined form of nitrogen in the ocean and this should have expanded the realm of the biosphere. Nitrogen fixation is strictly anaerobic (Postgate 1987; Zehr et al. 1995) and its origin may even predate the divergence of the three domains of life (Fani et al. 2000). After oxygenic photosynthesis arose (see below), nitrification must have become important. Nitrification is where ammonium ions are oxidized to nitrite and then nitrate by aerobic bacteria. Denitrification, the microbial reduction of $NO_3{}^-$ using organic matter to N_2O and N_2, completes the cycle. Thus after the $\sim$ 2.3 Ga rise of O_2 (Fig. 15.1), the nitrogen cycle was probably similar to today's.

The overall effect of early life, then, was to shift the atmosphere away from a state of modest chemical disequilibrium maintained by sunlight to a state of much greater disequilibrium.

15.3 Long-Term Climate Evolution and the Biosphere

Modification of the Earth's atmospheric composition by the biosphere would have affected greenhouse warming. Earth is warmed by absorption of low entropy visible and near-infrared radiation from the Sun and is cooled by emission of high entropy thermal infrared radiation. In between, the Earth and biosphere do dissipative work. If we treat the Earth as a blackbody with effective temperature T_e, the equilibrium energy flux balance is

$$S/4\,(1 - A) - \sigma\, T_e^4 = 0 \tag{15.3}$$

Here, $\sigma(= 5.67 \times 10^{-8}\,\mathrm{W/m^2/K^4})$ is the Stefan-Boltzmann constant, $S(= 1370\,\mathrm{W/m^2})$ is the solar flux at Earth's orbit, and A ($\cong 0.3$), is the planetary albedo, or reflectivity. Solving for the effective temperature yields $T_e = 255\,\mathrm{K}$. However, Earth is not a blackbody and the atmosphere warms the surface to temperature $T_s \sim 288\,\mathrm{K}$ through the greenhouse effect, which has a magnitude $\Delta T = T_e - T_s = 33\,\mathrm{K}$. Today H_2O vapor is responsible for about 2/3 of the greenhouse warming, while CO_2 accounts for much of the remainder. CH_4, N_2O, O_3, and anthropogenic chlorofluorocarbons contribute $\sim$ 2–3 K of the total.

The greenhouse effect should have been larger in the past (Sagan and Mullen 1972). Solar models indicate that the Sun was about 30% less bright when it formed 4.5 b.y. ago and that its luminosity has increased more or less linearly with time (Gough 1981). If one reduces S by 30% in (15.1), holding A and $\Delta\mathrm{T}_g$ constant, T_e drops to 233 K and $T_s = 266\,\mathrm{K}$, well below the freezing point of water. Actually, the problem is more severe if the strong temperature dependence of the water vapor content of air is included. Radiative-convective models suggest that T_s drops below the freezing point of water prior to $\sim$ 2 Ga ago, if the bulk gases of the atmosphere were constant. However, geologic evidence tells us that liquid water and life were both present back to at least 3.5 Ga (Sect. 15.2). The solution to this problem likely resides in increased concentrations of greenhouse gases. Indeed, there are good reasons why both CO_2 and CH_4 should have been more abundant in the deep past.

For CO_2, the argument involves the carbonate-silicate cycle (Walker et al. 1981; Berner et al. 1983). If the surface temperature were cold, the rate

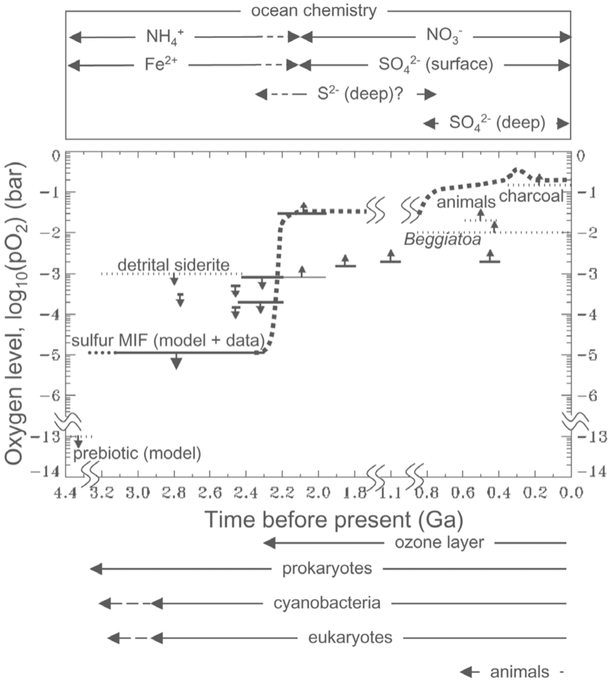

Fig. 15.2. The co-evolution of atmospheric O_2, ocean chemistry and life. The *thick dashed line* shows a possible evolutionary path for atmospheric O_2 that satisfies biogeochemical data. *Dotted horizontal lines* show the duration of biogeochemical constraints, such as the occurrence of detrital siderite ($FeCO_3$) in ancient riverbeds. Downward-pointing arrows indicate upper bounds on the partial pressure of oxygen (pO_2), whereas upward-pointing arrows indicate lower bounds. Unlabelled *solid horizontal lines* indicate the occurrence of particular paleosols (ancient soils), with the length of each line showing the uncertainty in the age of each paleosol. Inferences of pO_2 from paleosols are taken from Rye and Holland (1998). An upper bound on the level of pO_2 in the prebiotic atmosphere at c. 4.4 Ga (shortly after the Earth had differentiated into a core, mantle and crust) is based on photochemical calculations. MIF stands for "mass-independent isotope fractionation", which in sulfur is caused by photochemistry an O_2-poor atmosphere. The pO_2 level inferred from MIF observed in pre-2.4 Ga sulfur isotopes is based on the photochemical model results of Pavlov and Kasting (2002). Biological lower limits on pO_2 are based on the O_2 requirements of: (1) the marine sulfur-oxidizing bacterium, *Beggiatoa* (Canfield and Teske 1996); (2) animals that appear after 0.59 Ma (Runnegar 1991); (3) charcoal production in the geologic record. A "bump" in the oxygen curve around ∼300 Ma, in the Carboniferous, is based on the interpretation of Phanerozoic carbon and sulfur isotope data by Berner et al. (2000)

of silicate weathering would be low because of the dependence of chemical reaction rates on temperature and also as a result of low rainfall. Since weathering ordinarily removes CO_2, volcanic supply would increase the CO_2 concentration in the atmosphere. Eventually some surface temperature would be reached that supports rainfall and a carbon cycle. This feedback stabilizes global temperature on a timescale of 10^5–10^6 years.

Although CO_2 may have been somewhat higher, geological evidence shows that Earth's early atmosphere had very little O_2 until 2.3 Ga, and this implies that another greenhouse gas, methane, should have been predominant. Today biogenic methane is rapidly destroyed by oxidation, with a net reaction of $CH_4 + 2O_2 = CO_2 + H_2O$. Oxidation limits atmospheric methane to 1.7 ppmv. However, in the absence of O_2, methane would be long-lived and considerably more abundant. Photochemical models (Zahnle 1986; Pavlov et al. 2001) show that the lifetime of CH_4 in a low-O_2 atmosphere is $\sim$5,000–10,000 years, as opposed to $\sim$10 years today. Consequently, the present biological methane flux of 535 Tg CH_4/yr (Houghton 1994) could have supported an atmospheric CH_4 mixing ratio of $\sim$300 ppmv (Pavlov et al. 2001). The methane flux would likely have been substantial because the prebiotic H_2 mixing ratio would be $\sim 10^{-3}$ at steady-state with a balance of H_2 outgassing and escape to space. So CH_4 mixing ratios after methanogenesis evolved should have been roughly half of this, given efficient biological conversion by reaction (15.1). If CH_4 was an abundant constituent of the Archean atmosphere, then the greenhouse effect could have been large even if CO_2 concentrations were relatively modest (Pavlov et al. 2000) as geochemical evidence indicates (Rye et al. 1995; see also discussion in Catling et al. 2001).

15.4 Atmospheric Redox Change: The Rise of Oxygen

Abundant CH_4 in the early atmosphere comes at a price. Methane is photolyzed in the upper atmosphere by ultraviolet (UV) light below 145 nm wavelength. As a result hydrogen is liberated and escapes to space. Hydrogen escape oxidizes the Earth as a whole. Earth's hydrogen was not captured gravitationally from the solar nebula, so it ultimately comes from condensed materials such as hydrated silicates, organic compounds, and water ice. When hydrogen is lost from such materials, the residue is oxidized. Abundant atmospheric methane in the Archean would promote rapid escape of hydrogen to space, oxidizing the Earth, and it also would counteract the fainter sun by greenhouse warming. Thus, the major Earth history problems of the "faint young Sun" and "rise of O_2" are linked through methane (Catling et al. 2001).

Methanogenesis is a more ancient metabolism than oxygenic photosynthesis on the basis of genetic studies and biochemical complexity (e.g., Hedges et al. 2001). Before oxygenic photosynthesis evolved, methane would have been derived from the decomposition of organic matter made by anoxygenic photosynthesizers or chemoautotrophs. Such prokaryotes use H_2, reduced sulfur, or Fe^{2+} as electron donors (e.g., $2H_2S + CO_2 + h\nu \rightarrow CH_2O + H_2O + 2S$). CH_4 derived from such organic matter (via $2CH_2O = CH_4 + CO_2$) and subsequent H escape to space would cause oxidized sulfur or iron to be gained irreversibly by the crust or mantle given that the electron donor ultimately originates from the crust or mantle. Free O_2 is not produced. After the advent of oxygenic photosynthesis, a much larger supply of organic matter would have been available, and the methane flux to the atmosphere should have increased substantially. Given that reducing chemicals scavenged oxygen out of Archean atmosphere, paradoxically the immediate effect of the advent of oxygenic photosynthesis was probably an increase in atmospheric CH_4, promoting further oxidation of the Earth through H escape. Le Châtelier's principle[1] demands that atmospheric O_2 sinks decrease as the crust is irreversibly oxidized via CH_4-induced H escape. Inevitably, at some point O_2 was destined to flood the atmosphere.

The atmosphere started out with virtually no oxygen ($pO_2 \sim 10^{-13}$ bar) before life existed and probably had only a few ppmv in the late Archean (Pavlov and Kasting 2002). The subsequent rise of atmospheric O_2 at ~2.4–2.2 Ga irrevocably changed the course of biological evolution (Fig. 15.2). At ~2.4–2.2 Ga, the onset of red beds, oxidized soils, a step change in mass-independent sulfur isotopes, and the oxidative loss of detrital reduced minerals in riverbeds all indicate an "oxic transition" in the atmosphere (Catling and Kasting 2005). The partial pressure of oxygen (pO_2) is estimated to have been < 0.0008 atm before the transition and possibly > 0.03 atm afterwards (Rye and Holland 1998). Paleontology is consistent with the hypothesis that the rise of O_2 triggered biological evolution. The oldest fossils visible to the naked eye are the remains of a spiral seaweed, *Grypania spiralis* (Han and Runnegar 1992) from shales now dated at 1.87 Ga. Acritarchs, which are fossilized organic tests of unicellular algae, are first found in 1.8 Ga rocks in China and become abundant in younger rocks. Fossils that are 4–5 mm long are found in northern China at 1.7 Ga, and may be multicellular (Shixing and Huineng 1995). Then by 1.4 Ga, similar, often larger, carbonaceous fossils become abundant worldwide in marine sedimentary rocks. A subsequent increase in pO_2 at 1.0–0.64 Ga is inferred from an increase in sulfate in the ocean (Canfield and Teske 1996; Canfield 1998). The appearance of multicellular animals in the fossil record at ~0.6 Ga must have depended upon sufficient atmospheric O_2 as a precursor.

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[1] Le Châtelier's principle states that if a dynamic equilibrium is disturbed by changing conditions, the position of equilibrium moves to counteract the change. Atmospheric oxygen has a tendency to be removed by reaction with reducing gases released from the solid Earth (i.e., oxygen + reducing gases = oxidized gases). An irreversibly more oxidized crust and the consequent "stress" of the release of fewer reducing gases from the solid Earth would cause the atmospheric dynamic equilibrium to shift to the left according to Le Châtelier's Principle. This would produce higher oxygen levels.

Another important effect of the rise in O_2 at 2.4–2.2 Ga was to create a stratospheric ozone layer, shielding surface life from harmful UV radiation. Radiation below about 200 nm is strongly absorbed by CO_2 even in the absence of significant O_2, but ozone also shields biologically harmful radiation in the 200–300 nm range. Photochemical models show that harmful UV is mostly absorbed with an ozone layer that would form with O_2 levels about 1–3% of present (Kasting and Donahue 1980), similar to those inferred after 2.3 Ga (Fig. 15.2).

15.5 Oxygen, Energy, and Life

The increase in the amount of O_2 in the Earth's atmosphere gave organisms the potential for a much more energetic metabolism. Combined with evolution, this new energetic capability first produced larger organisms and ultimately organisms with differentiated anatomy, including brains and intelligence.

15.5.1 Aerobic Versus Anaerobic Energetics

Aerobic respiration provides about an order of magnitude more energy than anaerobic metabolisms. In living cells, energy is conserved first as adenosine triphosphate or ATP. ATP is used primarily in the synthesis of macromolecules and to drive active transport across cell membranes. The aerobic degradation of glucose, $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$ ($\Delta G^\circ = -2877\,\text{kJ/mol}$), yields 31 mol of ATP per mol glucose. The subsequent hydrolysis of ATP to provide energy has a free energy change of −29.3 kJ/mol. Thus, the efficiency of aerobic energy conversion is 32% ((29.3 kJ/mol ×31 mol)/ 2877 kJ)), with the other 68% lost as metabolic heat. In contrast, fermentative heterotrophic bacteria yield only ∼2–4 mol ATP per mol glucose. For example, the anaerobe *Lactobacillus* that turns milk sour ferments glucose to lactic acid ($C_6H_{12}O_6 = 2CH_3CHOHCOOH$, $\Delta G^\circ = -197\,\text{kJ/mol}$) yielding 2 mol of ATP. This implies a 30% efficiency ((29.3 kJ/mol ×2 mol)/ 197 kJ)), similar to aerobic metabolism, but produces only 1/16 of the energy of aerobic metabolism.

The significant lack of free energy in anaerobic metabolism precludes the capability for multicellular growth and multiple trophic levels. A useful generalization is that the growth yield per mol ATP is ∼ 10 g dry weight of organic matter (written as $Y_{\text{ATP}} = 10\,\text{g/mol}$ in bacteriology) (Bauchop and Elsden 1960; Russell and Cook 1995; Desvaux et al. 2001). For aerobic metabolism, 310 g ($31 \times Y_{\text{ATP}}$) of growth can be produced by ingesting 500 g of glucose (180 g/mol glucose + 310 g), which is a 63% (310/490) growth efficiency. In contrast, an average anaerobic metabolism producing 3 mol ATP per mol glucose, generates only 30 g of growth for an intake of 210 g, which is only a 14% growth efficiency. These numbers indicate the general relative growth efficiency between aerobic and anaerobic lifestyles, noting that measurements on higher animals show quite a range of 30–50% in growth efficiency (Brafield and Llewellyn 1982). The metabolic restriction on growth efficiency means that only aerobic organisms grow large. Aerobic respiration is efficient enough to allow eukaryotes to eat other organisms and grow large and multicellular in a hierarchical food chain. But anaerobic organisms are doomed to a unicellular lifestyle.

The evolution of metazoans required sufficient atmospheric O_2 not just for respiration but also for the synthesis of many essential biochemicals (Margulis et al. 1976). The latter includes sterols (e.g., cholesterol), polyunsaturated fatty acids that comprise membranes, the amino acids tyrosine and hydroxyproline, collagen (a hydroxyproline-containing structural protein) (Towe 1981), and biochemicals used in sclerotisation to harden cuticles (Brunet 1967). The first metazoans must have relied on O_2 diffusion. In conditions of low $O_2(\sim 1\%$ of present levels), these creatures were necessarily small ($< 0.5\,\mathrm{mm}$) because diffusion is proportional to the O_2 gradient from the exterior (Raff and Raff 1970; Runnegar 1982). Circulatory systems with respiratory proteins and mineral skeletons only evolved once O_2 levels were higher (Runnegar 1991). Metazoans emerged in a late burst of rapid diversification ~560–540 Ma ago (Ayala et al. 1998). This time is after a second increase in O_2 inferred from the geochemical record (Knoll 1992; Knoll and Holland 1995; Canfield and Teske 1996).

15.5.2 Why Complex Life Anywhere in the Universe Will Likely Use Oxygen

Free, diatomic oxygen (O_2) is clearly necessary for the growth and survival of terrestrial complex life. But is substantial free O_2 a universal requirement for complex life or is it merely peculiar to the vagaries of evolution on Earth? We can pose this question in another way: Given the need for a copious supply of energy by complex life, what is the most energetic chemical reaction available? Obviously, more energy is released if there are more reactants, so comparisons of energy release must be normalized per electron transfer. For any combination of elements in the periodic table, H-F and H-OH bonds have the highest bond enthalpies per electron (Table 15.1), giving the most energetic reactions per electron transfer. Table 15.1 compares terminal oxidants ranked according to the Gibb's free energy (ΔG^0) for reduction to an aqueous hydride. Because ΔG^0 ($= \Delta H^0 - T\varDelta S^0$) is dominated by enthalpy changes ($\varDelta H^0$), it generally tracks the hydride bond enthalpy. In the gas phase, oxygen is the next most energetic oxidant after fluorine, although in the aqueous phase (as shown), chlorine is marginally more energetic than oxygen. An extraterrestrial metabolism using fluorine would provide the most energy but for the fact that fluorine explodes in contact with organic matter.

Table 15.1. Comparison of possible terminal oxidants for biology. The list is ranked according to free energy of reduction to the aqueous hydride per electron under standard conditions, ΔG° (298.15 K, 1 atm)

Atom	Solar System abundance (% atoms)[a]	Redox reaction with hydrogen equivalent	ΔG^0 (kJ)[b]	Hydride bond enthalpy[c] per electron (kJ mol^{-1})	Reaction products with water	Prohibitive kinetic reactivity with organics?
F	2.7×10^{-6}	$\frac{1}{2}F_2 + \frac{1}{2}H_2 = HF(aq)$	−296.82	−282.5	O_2, HF	Yes
Cl	1.7×10^{-5}	$\frac{1}{2}Cl_2 + \frac{1}{2}H_2 = HCl(aq)$	−131.23	−215.5	HOCl	Yes
O	0.078	$\frac{1}{2}O_2 + \frac{1}{2}H_2 = \frac{1}{2}H_2O(l)$	−118.59	−231.5	-	No
Br	3.8×10^{-8}	$\frac{1}{2}Br_2 + \frac{1}{2}H_2 = HBr(aq)$	−103.96	−183.0	HOBr	Yes
N	0.01	$\frac{1}{6}N_2 + \frac{1}{2}H_2 + \frac{1}{3}H^+ = NH_4^+(aq)$	−26.44	−194.0	-	No
S	0.0017	$\frac{1}{2}S + \frac{1}{2}H_2 = \frac{1}{2}H_2S(aq)$	−13.92	−169.0	-	No
C	0.033	$\frac{1}{2}C + \frac{1}{2}H_2 = \frac{1}{4}CH_4(aq)$	−8.62	−206.0	-	No

a. Anders and Grevesse (1989).
b. Lide (1997).
c. Pauling (1960).

Fluorine also reacts with every other element apart from a few of the noble gases. Similarly, in water, chlorine and bromine form reactive sterilants: hypochlorous acid (HOCl) and hypobromous acid (HOBr), respectively. O_2 does not react with water but merely dissolves because its double bond provides greater stability than the single bonds in the halogens. In any case, a halogen-rich planetary atmosphere is simply ruled out because gases like fluorine or chorine would be removed extremely rapidly by gas-solid, gas phase or aqueous reactions. Given that F_2 and Cl_2 could never be abundant gases in a planetary atmosphere or plausible biological oxidants, one must conclude that the presence of free O_2 in a planetary atmosphere allows life to utilize the most efficient energy source per electron transfer available within the periodic table. This is undoubtedly a universal property because the periodic table and thermodynamics are universal. There are also two other reasons why complex life would use oxygen. First, O is third in cosmological abundance behind H and He (Anders and Grevesse 1989). Second, oxygen is found in water. Liquid water is required for Earth-like life (Kushner 1981) and its presence on a planet sets the conventional definition for planetary habitability (e.g., Catling and Kasting 2003). If a planet is habitable, with liquid H_2O and life, it has biological potential for accumulating O_2 in its atmosphere, since this comes from biological splitting of H_2O in photosynthesis. In turn, such a planet would also have the potential for complex life.

15.6 The Anomalous Nature of Earth's Current Atmosphere

Lovelock (1965) noted that the low entropy chemical state of Earth's atmosphere was a sign of life on the Earth's surface, cause by large gas fluxes from the biosphere. In essence, the atmosphere is an extension of the low entropy biosphere. For example, given $pO_2 \sim 0.209\,\text{bar}$, the thermodynamic equilibrium value of pCH_4 should be 10^{-145} bar. This means that there should not be a single molecule of CH_4 in Earth's oxygenated atmosphere at thermodynamic equilibrium. Instead, pCH_4 is $10^{-5.76}$ bar. As a life detection mechanism, however, there are potential ambiguities. Even an abiotic world would have chemical disequilibrium because free energy is supplied by solar energy, geothermal heat from radioactive decay, and tidal heating. Thus, chemical disequilibrium in a planetary atmosphere as a sign of life is a question of degree. The application of Maximum Entropy Production (MEP) to atmospheric chemistry may help us understand the distinction between biotic and abiotic planets.

I close this chapter with the further observation that Earth's atmosphere is physically anomalous. Whether life plays a part in this physical oddity (perhaps by affecting cloud or planetary albedo, for example, see Kleidon and Fraedrich, this volume) remains to be elucidated. The anomalous nature of Earth's atmosphere is a combination of the following three factors: Of planets with atmospheres, Earth is the sunniest in the Solar System (in terms of the flux on its surface) with the most unpredictable large-scale weather and the slowest atmospheric jets. Large-scale weather on other planets tends to be much more predictable. For example, the Red Spot of Jupiter is obviously highly predictable, having persisted for over 200 years. Similarly, Martian large-scale weather is sufficiently predictable that a hurricane-like weather system imaged by the Hubble Space Telescope was regenerated almost exactly about a year later, as imaged by the Mars Global Surveyor camera. Earth's unpredictable weather requires much more information for its description. Vern Suomi, the father of satellite meteorology first noted the jet stream paradox (Conway Leovy, personal communication), but it has not received any discussion in the literature. Suomi noticed that on planets from Earth to Neptune, the characteristic speed of the jets varies inversely with the available upward energy flux that drives the dynamics (Table 15.2). It is probably also important to realize that rates of kinetic energy dissipation are clearly low in the outer planet atmospheres but high in Earth's troposphere. Because of this, intuitively, it seems likely that this paradox will be explained through consideration of the principle of MEP.

Table 15.2. Suomi's paradox: The characteristic jet speed in planetary atmospheres *increases* despite a *decrease* of thermal forcing going from Earth to Neptune. (Courtesy of Conway Leovy)

Planet	Thermal Forcing [normalized to Earth]	Characteristic Jet Speed [m/s]
Earth	1.0	30
Mars	0.09	80
Jupiter	0.05	100
Saturn	0.02	150
Uranus, Neptune	0.003	300

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