

Simon Fraser University
Geochemistry

Stephen Lower

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CHAPTER OVERVIEW

1: The Earth and its Lithosphere

- 1.1: Composition and Structure of the Earth
- 1.2: Origin of the Elements
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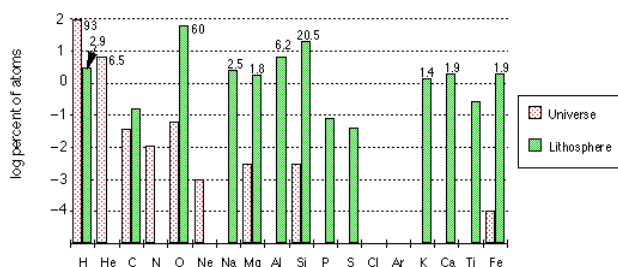
1.1: Composition and Structure of the Earth

The earth has been in a state of continual change since its formation. The major part of this change, involving volcanism and tectonics, has been driven by heat produced from the decay of radioactive elements within the earth. The other source of change has been solar energy, which acts as the driving force of weathering and is the ultimate source of energy for living organisms.

The solar system was probably formed about 4.6 billion years ago, and the oldest known rocks have an age of 3.8 billion years. There is thus a gap of 0.8 billion years for which there is no direct evidence. It is known that the earth was subjected to extensive bombardment earlier in its history; recent computer simulations suggest that the moon could have resulted from an especially massive collision with another body. Although these major collisions have diminished in magnitude as the matter in the solar system has become more consolidated, they continue to occur, with the most recent one being responsible for the annihilation of the dinosaurs and much of the other life on Earth. The lack of many overt signs of these collisions (such as craters, for example) testifies to the dynamic processes at work on the Earth's surface and beneath it.

Chemical Composition of the Earth

The earth is composed of 90 chemical elements, of which 81 have at least one stable isotope. The unstable elements are ^{43}Tc and ^{61}Pm , and all elements heavier than ^{83}Bi .



Note that the vertical axis is logarithmic, which has the effect of greatly reducing the visual impression of the differences between the various elements.

The chart gives the abundances of the elements present in the solar system, in the earth as a whole, and in the various geospheres. Of particular interest are the differences between the terrestrial and cosmic abundances, which are especially notable in the cases of the lighter elements (H, C, N) and the noble gas elements (He, Ne, Ar, Xe, Kr).

Example 1.1.1

Given the mix of elements that are present in the earth, how might they combine so as to produce the chemical composition we now observe?

Solution

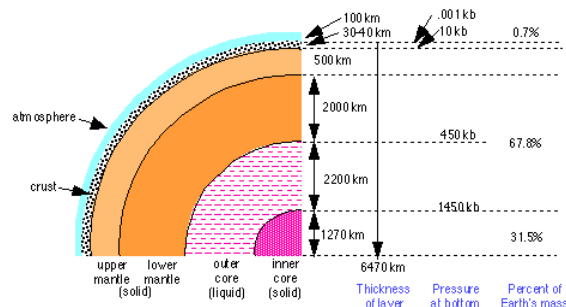
Given the mix of elements that are present in the earth, how might they combine so as to produce the chemical composition we now observe? Thermodynamics allows us to predict the composition that any isolated system will eventually reach at a given temperature and pressure. Of course the earth is not an isolated system, although most parts of it can be considered approximately so in many respects, on time scales sufficient to make thermodynamic predictions reasonably meaningful. The equilibrium states predicted by thermodynamics differ markedly from the observed compositions. The atmosphere, for example, contains 0.03% CO_2 , 78% N_2 and 21% O_2 ; in a world at equilibrium the air would be 99% CO_2 .

Similarly, the oceans, containing about 3.5% NaCl , would have a salt content of 35% if they were in equilibrium with the atmosphere and the lithosphere. Trying to understand the mechanisms that maintain these non-equilibrium states is an important part of contemporary environmental geochemistry.

Structure of the Earth

Studies based on the reflection and refraction of the acoustic waves resulting from earthquakes show that the interior of the earth consists of four distinct regions. A combination of physical and chemical processes led to the differentiation of the earth into these

major parts. This is believed to have occurred approximately 4 billion years ago.



The Earth's Core

The Earth's core is believed to consist of two regions. The inner core is solid, while the outer core is liquid. This phase difference probably reflects a difference in pressure and composition, rather than one of temperature. Density estimates obtained from seismological studies indicate that the core is metallic, and mainly iron, with 8-10 percent of lighter elements.

Hypotheses about the nature of the core must be consistent with the core's role as the source of the earth's magnetic field. This field arises from convective motion of the electrically conductive liquid comprising the outer core. Whether this convection is driven by differences in temperature or composition is not certain. The estimated abundance of radioactive isotopes (mainly U^{238} and K^{40}) in the core is sufficient to provide the thermal energy required to drive the convective dynamo. Laboratory experiments on the high-pressure behavior of iron oxides and sulfides indicate that these substances are probably metallic in nature, and hence conductive, at the temperatures (4000-5000K) and pressures (1.3-3.5 million atm) that are estimated for the core. Their presence in the core, alloyed with the iron, would be consistent with the observed density, and would also resolve the apparent lack of sulfur in the earth, compared to its primordial abundance.

The mantle

The region extending from the outer part of the core to the crust of the earth is known as the *mantle*. The mantle is composed of oxides and silicates, i.e., of rock. It was once believed that this rock was molten, and served as a source of volcanic magma. It is now known on the basis of seismological evidence that the mantle is not in the liquid state. Laboratory experiments have shown, however, that when rock is subjected to the high temperatures and pressures believed to exist in the mantle, it can be deformed and flows very much like a liquid.

The upper part of the mantle consists of a region of convective cells whose motion is driven by the heat due to decay of radioactive potassium, thorium, and uranium, which were selectively incorporated in the crystal lattices of the lower-density minerals that form the mantle. There are several independent sources of evidence of this motion. First, there are gravitational anomalies; the force of gravity, measured by changes in elevation in the sea surface, is different over upward and downward moving regions, and has permitted the mapping of some of the convective cells. Secondly, numerous isotopic ratio studies have traced the exchange of material between oceanic sediments, upper mantle rock, and back into the continental crust, which forms from melting of the upper mantle. Thirdly, the composition of the basalt formed by upper mantle melting is quite uniform everywhere, suggesting complete mixing of diverse materials incorporated into the mantle over periods of 100 million years.

High-pressure studies in the laboratory have revealed that olivine, a highly abundant substance in the mantle composed of Fe, Mg, Si, and O (and also the principal constituent of meteorites) can undergo a reversible phase change between two forms differing in density. Estimates of conditions within the upper mantle suggest that this phase change could occur within this region in such a way as to contribute to convection. The most apparent effect of mantle convection is the motion it imparts to the earth's crust, as evidenced by the external topography of the earth.

The crust

The outermost part of the earth, known also as the lithosphere, is broken up into plates that are supported by the underlying mantle, and are moved by the convective cells within the mantle at a rate of a few centimetres per year. New crust is formed where plates move away from each other under the oceans, and old crust is recycled back into the mantle as where plates moving in opposite directions collide.

The oceanic crust

The parts of the crust that contain the world's oceans are very different from the parts that form the continents. The continental crust is 10-70 km thick, while oceanic crust averages only 5-7 km in thickness. Oceanic crust is more dense ($3.0\text{-}3.1\text{ g cm}^{-3}$) and therefore "floats" on the mantle at a greater depth than does continental crust (density $2.7\text{-}2.8$). Finally, oceanic crust is much younger; the oldest oceanic crust is about 200 million years old, while the most ancient continental rocks were formed 3.8 billion years ago.

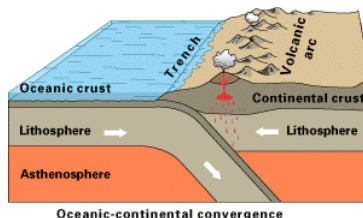
New crust is formed from molten material in the upper mantle at the divergent boundaries that exist at undersea ridges. The melting is due to the rise in temperature associated with the nearly adiabatic decompression of the upper 50-70 km of mantle material as separation of the plates reduces the pressure below. The molten material collects in a magma pocket which is gradually exuded in undersea lava flows. The solidified lava is transformed into crust by the effects of heat and the action of seawater which selectively dissolves the more soluble components.



An animated view of seafloor spreading.

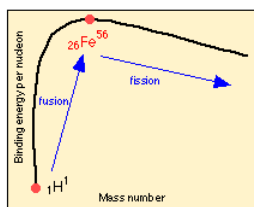
Plate collisions

Where two plates collide, one generally plunges under the other and returns to the mantle in a process known as **subduction**. Since the continental plates have a lower density, they tend to float above the oceanic plates and resist subduction. At continental boundaries such as that of the North American west coast where an oceanic plate pushes under the continental crust, oceanic sediments may be sheared off, resulting in a low coastal mountain range (see here for a nice animation of this process.) Also, the injection of water into the subducting material lowers its melting point, resulting in the formation of shallow magma pockets and volcanic activity. Divergent plate boundaries can cross continents, however; temporary divergences create rift valleys such as the Rhine and Rio Grande, while permanent ones eventually lead to new oceanic basins.



Collision of two continental plates can also occur; the most notable example is the one resulting in the formation of the Himalayan mountain chain.

The Earth is composed of 90 chemical elements, of which 81 have at least one stable isotope. Most of these elements have also been detected in stars. Where did these elements come from? The accepted scenario is that the first major element to condense out of the primordial soup was helium, which still comprises about one-quarter of the mass of the known universe.

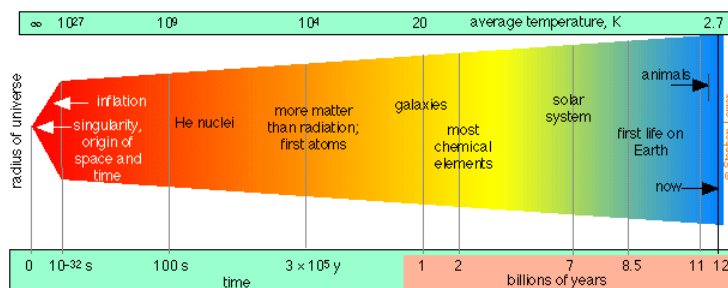


Hydrogen is the least thermodynamically stable of the elements, and at very high temperatures will combine with itself in a reaction known as *nuclear fusion* to form the next element, $^4\text{He}^2$. "Heavier" nuclei (that is, those having high atomic numbers, indicated here by the subscript preceding the element symbol), are more stable than "lighter" ones, so this fusion process can

continue up to ${}_{56}\text{Fe}$, which is the most energetically stable of all the nuclides. Beyond this point, heavier nuclei slowly become less stable, so fission becomes more likely. Fission, however, is not considered an important mechanism of primordial nucleosynthesis, so other processes are invoked, as discussed farther below.

Primordial Chemistry

According to the “big bang” theory for which there is now overwhelming evidence, the universe as we know it (that is, all space, time, and matter) had its origin in a point source or *singularity* that began an explosive expansion about 12-15 billion years ago, and which is still continuing.



Following a brief period of extremely rapid expansion called *inflation*, protons and neutrons condensed out of the initial quantum soup after about 10^{-32} s. Helium and hydrogen became stable during the first few minutes, along with some of the very lightest nuclides up to ${}_{7}\text{Li}$, which were formed through various fusion and neutron-absorption processes. Formation of most heavier elements was delayed for about 10^6 years until nucleosynthesis commenced in the first stars. Hydrogen still accounts for about 93% of the atoms in the universe.

The main lines of observational evidence that support this theory are the 2.7K background radiation that permeates the cosmos (the cooled-down remnants of the initial explosion), and the abundances of the lightest elements. Conventional physics is able to extrapolate back to about the first 10^{-33} second; what happened before then remains speculative.

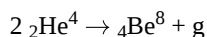
Stellar nucleosynthesis

All elements beyond hydrogen were formed in regions where the concentration of matter was large, and the temperature was high; in other words, in stars. The formation of a star begins when the gravitational forces due to a large local concentration of hydrogen bring about a contraction and compression to densities of around 10^5 g cm^{-3} . This is a highly exothermic process in which the gravitational potential energy is released as heat, about 1200 kJ per gram, raising the temperature to about 10^7 K . Under these conditions, hydrogen nuclei possess sufficient kinetic energy to overcome their electrostatic repulsion and undergo nuclear fusion:

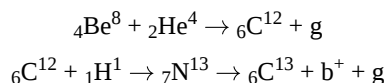


Hydrogen burning

There will be a net mass loss in above process, which will therefore be highly exothermic and is known as “hydrogen burning”. As hydrogen burning proceeds, the helium collects in the core of the star, raising the density to 10^8 g cm^{-3} and the temperature to 10^8 K . This temperature is high enough to initiate *helium burning*, which proceeds in several steps:



The first product, ${}_4\text{Be}^8$ has a half life of only 10^{-16} sec, but a sufficient amount accumulates to drive the following two reactions:



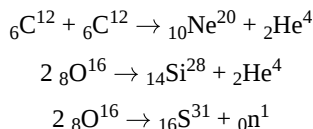
The size of a star depends on the balance between the kinetic energy of its matter and the gravitational attraction of its mass. As the helium burning runs its course, the temperature drops and the star begins to contract. The course of further nucleosynthesis and the subsequent fate of the star itself depends on the star’s mass.

Small stars

If the mass of the star is no greater than 1.4 times the mass of our sun, the star collapses to a white dwarf, and eventually cools to a dark, dense dead star.

Big stars

In larger stars, the gravitational forces are sufficiently strong to overcome the normal repulsion between atoms, and so gravitational collapse continues. The gravitational energy released in this process produces temperatures of 6×10^8 K, which are sufficient to initiate a complex series of nuclear reactions known as the *carbon-nitrogen cycle*. The net reaction of this cycle is the further fusion of hydrogen to helium, in which C^{12} acts as a catalyst, and various nuclides of nitrogen and oxygen are intermediates. The temperature is sufficiently high, however, to initiate fusion reactions of some of these intermediates:

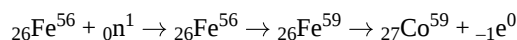


Supernovas

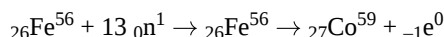
The intense gamma radiation that is produced in some of these reactions breaks some of the product nuclei into smaller fragments, which can then fuse into a variety of heavier species, up to the limit of ${}_{26}Fe^{56}$, beyond which fusion is no longer exothermic. The greater relative abundance of elements such as ${}_6C^{12}$, ${}_8O^{16}$, and ${}_{10}Ne^{20}$ which differ by a ${}_2He^4$ nucleus, reflects the participation of the latter species in these processes. These exothermic reactions eventually produce temperatures of 8×10^9 K, while contraction continues until the central core is essentially a ball of neutrons having a radius of about 10 km and a density of 10^{14} g cm⁻³. At the same time the outer shell of the star is blasted away in an explosion known as a *supernova*.

Since ${}_{26}Fe^{56}$ has the highest binding energy per nucleon of any nuclide, there are no exothermic processes which can lead to the formation of heavier elements. Fusion into heavier species is also precluded by the electrostatic repulsion of the highly charged nuclei. However, the process of neutron capture can still take place (this is the same process that is used to make synthetic elements). The neutrons are by-products of a large variety of stellar processes, and are present in a wide range of energies. Two general types of neutron capture processes are recognized. In an “s” (slow) process, only a single neutron is absorbed and the product usually decomposes by β -decay into a more proton-rich species.

Elements heavier than iron



This process occurs at rates of about 10^5 yr⁻¹, and accounts for the lighter isotopes of many elements. The other process (the “r”, or rapid process) occurs in regions of high neutron density and involves multiple captures at rates of 0.1-10 sec⁻¹:



This mechanism favors the heavier, neutron-rich isotopes and the heaviest elements.

Other elements

A few nuclei are not accounted for by any of the processes mentioned. These are all low-abundance species, and they probably result from processes having low rates. Examples are Sn^{112} and Sn^{114} which may be produced through proton-capture, and H^2 , Li^6 , Li^7 , Be , B^{10} and B^{11} , which may come from spallation processes resulting from collisions of cosmic ray particles with heavier elements

Formation of the solar system

The solar system is believed to have formed about 5 billion years ago as a result of aggregation of cosmic dust and interstellar atoms in a region of space in which the density of such material happened to be greater than average. Over 99.8% of this mass, which consisted mostly of hydrogen, collapsed into a proto-sun; the gravitational energy released in this process raised the temperature sufficiently to initiate the hydrogen fusion reactions discussed above.

The planets

The remaining material probably formed a disk that rotated around the sun. As the temperature dropped to around 2000K, some of the most stable combinations of the elements began to condense out. These substances might have been calcium aluminum silicates, followed by the more volatile iron-nickel system, and then magnesium silicates. The further aggregation of these materials, together with the other constituents of the cooling disk, is now believed to be the origin of the planets. Density estimates

indicate that the planets closest to the sun are predominantly rocky in nature, and probably condensed first. The outer planets (Uranus, Neptune and Pluto) appear to consist largely of water ice, methane, and ammonia, with a smaller rocky core.

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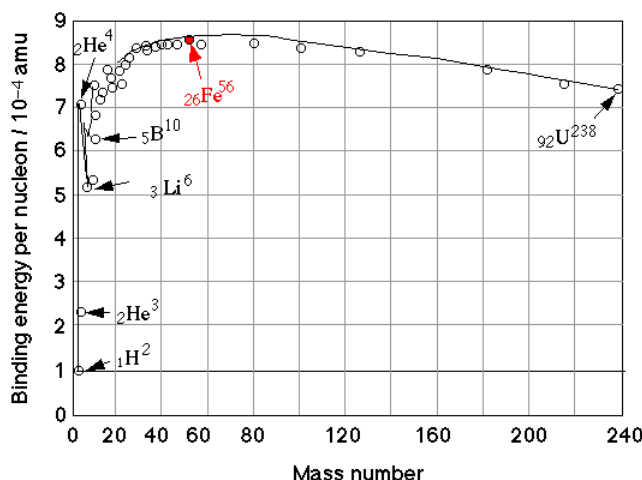


Figure 1.2.1: Hydrogen is the least thermodynamically stable of the elements, and at very high temperatures will combine with itself in a reaction known as *nuclear fusion* to form the next element, ²He⁴. "Heavier" nuclei (that is, those having high atomic numbers, indicated here by the subscript preceding the element symbol), are more stable than "lighter" ones, so this fusion process can continue up to ⁵⁶Fe, which is the most energetically stable of all the nuclides. Beyond this point, heavier nuclei slowly become less stable, so fission becomes more likely. Fission, however, is not considered an important mechanism of primordial *nucleosynthesis*, so other processes are invoked, as discussed farther below.

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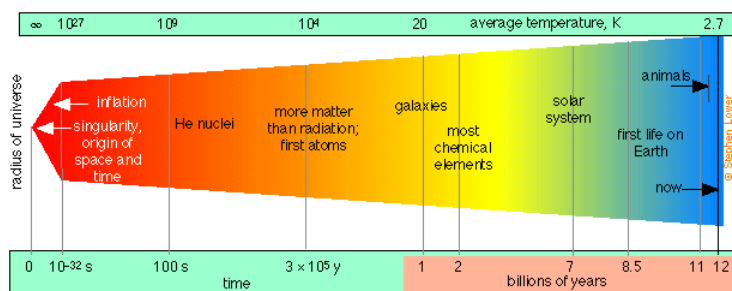


Figure 1.2.2

Following a brief period of extremely rapid expansion called *inflation*, protons and neutrons condensed out of the initial quantum soup after about 10⁻³² s. Helium and hydrogen became stable during the first few minutes, along with some of the very lightest nuclides up to ⁷Li, which were formed through various fusion and neutron-absorption processes. Formation of most heavier elements was delayed for about 10⁶ years until nucleosynthesis commenced in the first stars. Hydrogen still accounts for about 93% of the atoms in the universe.

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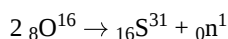
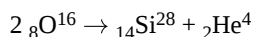
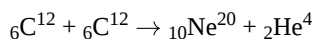
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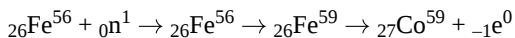
Only six supernovas have been observed in our galaxy. The supernova of 1987 was the most recent; the one before this occurred in 1604, prior to the invention of the telescope. Tycho Brahe's observation of a supernova in 1572 was crucial in overturning the Aristotelian tradition of the immutability of the "fixed stars", or "firmament". The remains of these supernovas have been detected and studied by X-ray observations.

Thus all of the elements in our solar system that are heavier than iron are the recycled remnants of former stars.

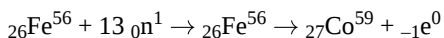
The [Chandra X-ray observatory page on supernovas](https://chandra.harvard.edu/observatory/supernovas.html)

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Contributors

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1.3: Formation and evolution of the Earth

The solar system is believed to have formed about 5 billion years ago as a result of aggregation of cosmic dust and interstellar atoms in a region of space in which the density of such material happened to be greater than average. Over 99.8% of this mass, which consisted mostly of hydrogen, collapsed into a proto-sun; the gravitational energy released in this process raised the temperature sufficiently to initiate the hydrogen fusion reactions discussed above.

The planets

The remaining material probably formed a disk that rotated around the sun. As the temperature dropped to around 2000K, some of the most stable combinations of the elements began to condense out. These substances might have been calcium aluminum silicates, followed by the more volatile iron-nickel system, and then magnesium silicates. The further aggregation of these materials, together with the other constituents of the cooling disk, is now believed to be the origin of the planets. Density estimates indicate that the planets closest to the sun are predominantly rocky in nature, and probably condensed first. The outer planets (Uranus, Neptune and Pluto) appear to consist largely of water ice, methane, and ammonia, with a smaller rocky core.

Formation of the Earth

The Earth formed by accretion of solid and particulate material that remained after the much more massive amounts of hydrogen and helium present in the original protoplanets had been dispersed out of the solar system. Gradually, the heat produced by decay of radioactive elements brought about partial melting of the silicate rocks; these lower density molten materials migrated upward, leaving the more dense, iron-containing minerals below. This process, which took about 2 million years, was the first of the three stages into which the chemical evolution of the earth is usually divided:

1. **Primary differentiation** of the elements between the core and mantle.
2. **Secondary differentiation** of the elements, reflecting relative ionic sizes, bonding properties, and solubilities (influencing phase behavior such as fractional crystallization, etc.)
3. **Tertiary differentiation**, still operative, involving the interaction of the crust with the hydrosphere and atmosphere.

The above listing should not be taken too literally; all three kinds of processes have probably proceeded simultaneously, and over a number of cycles. Since the earth is losing approximately four times as much heat as is generated by radioactive decay, the principal driving force of primary and secondary differentiation has gradually slowed down. Partial melting of the upper mantle brought about further fractionation as silicon-containing materials of low density migrated outward to form a crust. In its early stages the stronger granitic rocks had not yet appeared, and the crust was mechanically weak. Upwelling flows of lava would break the surface, and the weight of the solidified lava would cause the crust to subside. In some places, magma would solidify underground, forming low-density rock (batholiths) that would eventually rise by buoyancy and push up overlying crust. These mountain-building periods probably occurred in 6-8 major episodes, each lasting about 800 million years.

Rain

At the same time, outgassing of solids released large amounts of HCl, CO, CO₂, H₂S, CH₄, SO₂, and SO₃ into the primitive atmosphere. Large amounts of water were present in the primeval rocks in the form of hydrates, which were broken down as the result of the heating. Eventually when the outer crust cooled enough to permit condensation of the water vapor as rain, a new stage of chemical evolution began. The rain was initially highly acidic, equivalent to about 1M HCl; this reacted readily with the basic rocks having high contents of K, Na, Mg, and Ca, leaching them away and forming what would eventually evolve into the oceans. The partial dissolution of the rocks also resulted in large amounts of sediments, which played their own role in the transformation of the earth's surface.

The continents

Within the crust, the lighter materials, being in isostatic equilibrium with the upper mantle, floated higher, and gradually became the nuclei of continents, which grew by accumulating similar material around their boundaries. This picture of continental development is supported by isotopic ratio studies which indicate that the nucleus of the North American continent, the Canadian Shield, is over 2.5 billion years old, while the peripheral parts are less than 0.6 billion years of age.

Primary differentiation of the elements

The more traditional geochemical view of primary differentiation begins with the assumption that the core of the earth is in a chemically reduced state, while the metallic elements constituting the mantle are almost entirely oxidized to their lower free energy

cationic forms. Oxygen and sulfur acted as the major electron acceptors in this process, but the abundance of these elements was insufficient to oxidize much of the nickel or iron.

Iron as a reductant

Iron itself is believed to have played a crucial role in the primary differentiation of other metals and of oxidized metallic elements that iron is able to reduce. As the dense molten iron migrated in toward the core, it dissolved (formed a liquid alloy with) any other metals with which it came in contact, and it reduced (donated electrons to) those metallic cations that are less “active” metals than iron under these conditions. The resulting metal would then mix with more of the migrating liquid iron, and be carried along with it into the core.

Redox power of the elements

Accordingly, elements whose reduction potentials are more positive than iron (i.e., are lower-free energy electron sinks) are called *siderophiles*; these elements have a low abundance in the crust and upper mantle. The other two important classes of solid-forming elements are *lithophile* and *chalcophile* (see below.) These generally have more negative reduction potentials than iron, and are distinguished mainly by their relative affinity for oxygen or sulfur. The chalcophiles, of which Cu, Cd, and Sb are examples, tend to form larger, more polarizable ions which can associate with the sulfide ion. The lithophiles comprise those elements such as K, Al, Mn, and Si, which have smaller ions and which combine preferentially with oxygen. This broad classification is reflected in the dominant forms in which many of these elements occur in nature.

Secondary differentiation of the elements

The differential distribution of the elements within one of the main regions of the earth has been studied in detail only in that portion that is accessible, namely the upper crust. It is clear that fractional crystallization from the cooling magma has played an important role. The relative temperatures at which minerals crystallize is determined in large part by their lattice energies, which are in turn related to ionic sizes and charges. Minerals with small, highly charged ions will have higher melting points and should crystallize first. Thus the sodium-containing feldspar albite ($\text{NaAlSi}_3\text{O}_8$) is found nearer the surface than is its calcium analog anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The less abundant elements often do not form minerals of their own, but may replace the ion of a more abundant mineral in its crystal lattice. This is known as *isomorphous replacement*, and it naturally depends on the relative ionic radii. Some ion pairs that undergo isomorphous replacement in minerals are K^+ and Ba^{2+} , Si^{4+} and Ge^{4+} .

Phase behavior

The Phase Rule can be invoked to explain in a very rough way the differentiation of the elements into distinct solid phases.

$$P = C + 2 - F$$

Taking the degrees of freedom as 2 (fixed temperature and pressure), the six major elemental components (O, Si, Al, Fe, Mg and Na) can form up to six phases. Actually, more than 99% of igneous rocks comprise seven principal mineral phases. These are: the silica minerals, feldspars, feldspathoids, olivine, pyroxenes, amphiboles and micas.

The differential deposition of minerals is also influenced by the temperature-composition phase relations as exemplified by the ordinary two-component phase diagram. If the mineral that is rich in one component and which first crystallizes out is also more dense, then the richer ore will occur near the bottom of the deposit, while a more mixed ore (approaching the eutectic) will remain near the top.

Geochemical classification of the elements

Whether an element is concentrated in the crust or elsewhere depends on its chemical behavior and on the physical properties of its stable compounds. Geochemists have found it convenient to establish the following general classifications:

- *lithophiles* (“rock-loving”) elements are those such as Fe, Al, and Si which tend to occur as oxides (and to a lesser extent as chlorides and carbonates.) Elements in this, the largest of all the groups, are concentrated in the crust.
- *chalcophiles* also occur in the crust, but mainly in combination with sulfur and the other chalcogen elements of Groups 15-16.
- *siderophiles* refer to the elements such as Ni which have concentrated in the core along with Fe.
- *atmosphiles* consist of N, H and their volatile compounds and the noble gases which concentrate in the atmosphere.

1.4: The Earth's crust

The structure and composition of the outer part of the lithosphere has been profoundly affected by interactions with the atmosphere over one-quarter of the surface area of the earth, and with the hydrosphere over the remaining area. Further modification of the outermost parts of the crust has occurred as the result of the activities of living organisms. These changes have transformed much of the outermost parts of the crust into an unconsolidated surface region called the regolith. Further weathering and translocation of soluble substances often results in a sequence of horizons consisting of sediments, soils, or evaporites.

Chemically, the earth's crust consists of about 80 elements distributed in approximately 2000 compounds or minerals, many of which are of variable composition. Over 99% of the mass of the crustal material is made up of only eight of these elements, however:

Table 1.4.1: Average amounts of elements in crustal rocks, mg/g.

O	466,000	Na	28,300
Si	277,200	K	25,900
Al	81,300	Mg	20,900
Fe	50,000	Ti	4,400
Ca	36,300	H	1,400

The crust has its origin in the upwelling convection currents that bring mantle material near to the surface at the mid-ocean ridges. The reduced pressure causes it to melt into *magma*. The magma may solidify before it reaches the surface, forming basalt, or it may emerge from the surface in a volcanic eruption. The oceanic crust consists mostly of the simpler silicate minerals, which are said to be *basic* or *mafic*. The more evolved, silicon-rich rocks found in the continental crust are known as *acidic* or *sialic*.

Oceanic crust is continually being extruded from regions of the plastic mantle that intrude upward to just beneath the ocean's floor at the mid-ocean ridges. A corresponding amount of this crust is being returned to the lithosphere at subduction zones off the West coasts of the Americas, and in the process pushing up the mountain ranges that lie along these coasts. The subducted oceanic crust is reheated and combined with sedimentary material to undergo partial remelting and reworking; this is believed by some to be the origin of *granite*. Subduction proceeds at a rate of a few cm per year, and the complete cycle time is on the order of a few hundred million years.

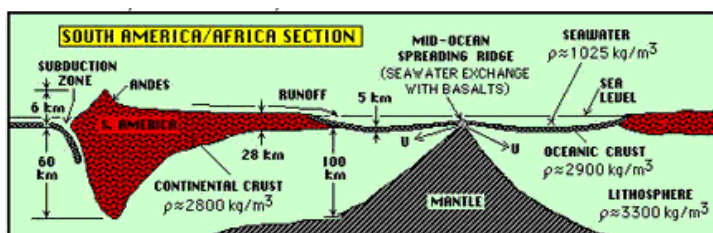


Figure 1.4.1: The continental and oceanic crusts. This schematic cross section runs in a west-to-east direction, from just off the West coast of South America on the left to the African continent on the right. Oceanic crust is shown in black, with continental crust in red. (From Cosmos and Earth Study Guide, NYU)

Both oceanic and continental crusts float on the more dense upper lithosphere, and gradually shift their positions as they push against each other, and in response to the slow convective motions in the medium that supports them. The **continental crust** is thicker than the oceanic crust, but it is also less dense, which allows it to float higher (and thus to differentiate continents from oceans.) The lower density also prevents it from being subducted. Recycling can occur indirectly as continental material erodes and is deposited as sediments on the ocean floor, but this is a much slower process and one that takes billions instead of millions of

years. Some of the very oldest rocks, found in Greenland and Labrador, have been dated at 3.9 billion years, and thus approach the age of the Earth itself.

Chemistry of the crust

When magma crystallizes it forms igneous rock, the major component of the Earth's crust. The crystallization is a complex process which is not entirely understood, due largely to the lack of sufficient thermodynamic data on the various components at high temperatures and pressures. It is known that the different components of magma have differing melting points and densities, and that the phase behavior of multicomponent systems based on some of these substances is quite complex, involving binary and ternary eutectics, solid solutions, the presence of dissolved water (under pressure), and incongruent melting. One consequence of this complexity is that the composition of the magma will change as crystallization takes place; different substances will crystallize at various stages, and the resulting solids may migrate toward the top or bottom of the region if their densities differ greatly from that of the magma

It is well known that larger crystals form when a melt cools more slowly. This principle affords a simple distinction between the coarser-grained plutonic rocks, which are believed to have been formed by gradual cooling of magma pockets within the crust, and the fine-grained volcanic rocks such as basalt. Under the influence of heat and pressure, particularly at plate boundaries, solid crustal material may undergo partial or complete remelting, followed by cooling and transformation into metamorphic rocks such as gneiss, micas, quartzite, and possibly granites.

***Granite** was once thought to be an igneous rock, originating from the crystallization of a particular kind of magma. The association of granitic rocks with mountainous regions, and the similarity of their compositions in widely scattered regions, lends credence to the more recent hypothesis that granitic rocks are of metamorphic origin.*

Another class of rock is *sedimentary rock*, formed from the consolidation of material produced by weathering and other chemical, and biological processes. Sedimentary rocks cover about three-quarters of the land area of the earth; 80% are shales, 15% sandstones and 5% limestones.

Composition of rock

The chemical composition of rocks tends to be complex and variable, and can only be specified in a precise way at the structural level. The traditional way of expressing rock compositions is in terms of the mass percent of the oxides of the elements present in the rock.

Table 1.4.1: : Chemical composition of a typical rock (quartz-feldspar-biotite gneiss). The figures are in percent by weight.

common name	fresh rock	weathered rock
Silica SiO ₂	71.54	70.30
Alumina Al ₂ O ₃	14.62	18.34

common name	fresh rock	weathered rock
Ferric oxide Fe_2O_3	0.69	1.55
Ferrous oxide FeO	1.64	0.22
Magnesia MgO	0.77	0.21
Quartz SiO_2	2.08	0.10
Soda Na_2O	3.84	0.09
Potash K_2O	0.32	5.88
Water H_2O	0.32	5.88
Others	0.65	0.54
Total	100.07	99.70

This does not mean that these oxides, or the structural units they represent, are actually present as such in a rock. In the chemical analysis of rocks, oxygen is generally not determined separately. When it is, however, it is found in an amount that would be expected to combine stoichiometrically with the other elements present. Thus the composition of albite can be written as either $\text{NaAlSi}_3\text{O}_8$ or $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Some rocks contain varying ratios of certain elements. For example olivine, which can be

considered a solid solution of Mg_2SiO_4 and Fe_2SiO_4 , can be represented by $(\text{Mg,Fe})_2\text{SiO}_4$; this implies that the ratio of metal to silica is constant, and that magnesium is ordinarily present in greater amount than iron.

The major structural elements of rock (both in the crust and in the mantle) are the silicate minerals, built from silicon atoms surrounded tetrahedrally by four oxygens. The simplest of these consist just of SiO_4^{4-} tetrahedra interspersed with positive ions to achieve electroneutrality; olivine, $(\text{Mg,Fe})_2\text{SiO}_4$ is a well known example. More commonly, the silicate groups polymerize by sharing one or more oxygen atoms at adjacent tetrahedral corners. Depending on the number of joined corners per silicate unit, this can lead to the formation of a wide variety of chains (pyroxenes, amphiboles) and sheets (micas), culminating in the complete tetrahedral polymerization that produces quartz, SiO_2 .

Higher degrees of polymerization are associated with higher ratios of Si to O, smaller quantities of positive ions, and higher melting points. Thus when magma cools, the first silicates to crystallize are the olivines, followed by chain and sheet minerals having progressively higher degrees of polymerization and smaller fractions of cations of metals such as Fe and Mg.

Distribution of elements; ores

Although some elements are distributed fairly uniformly throughout the crust, others occur at greatly enhanced concentrations in localized areas. There are two general processes that result in these localized excesses, which are called *ores* when their extraction and refining is economically feasible

The first of these relates to how well a metallic ion can fit into the silicate lattice structure. Ions having the right charge and size can readily enter this structure, displacing the more common ions of Fe, Al and Mg. Such ions (of which Ga^{3+} is an example) are readily soluble in other minerals and thus are widely distributed and do not concentrate into ores. Other ions may be too large (Cs and La), too small (Li, Be, B) or too highly charged (Nb, Ta, W) to be accommodated in silicate mineral structures; these elements tend to remain in the magma as it solidifies, finally forming solid minerals only in the last stages of cooling.

The other major source of ores is *hydrothermal* formation. Magma contains some water itself, and additional water from the surface is able to reach the heated rock near magma chambers. At the very high temperatures and pressures that prevail in these regions, the water can dissolve many compounds such as sulfides which are normally considered highly insoluble. When these superheated solutions rise to the surface the solids are re-deposited, often in highly concentrated form. Ores of Cu, Sn, W, and possibly some iron ores, as well as some native metals such as gold, are believed to be formed in this way.



Figure 1.4.2: The hydrothermal vent photographed here emits both black and white "smoke".

Hydrothermal vents known as "black smokers" have been observed at sites of sea-floor spreading; the "smoke" consists of metallic sulfides which precipitate in the cold seawater. The veins of pyrites (FeS_2) and similar sulfide minerals that are often observed in rock formations are the result of hydrothermal solutions that once penetrated cracks and fissures in the rock.

[Deep-sea hydrothermal vents](#) (many more pictures)

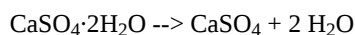
[Theories of ore formation](#) (a more technical tutorial)

Chemical weathering

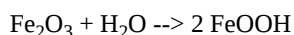
The weathering of rocks at the earth's surface is a complex process involving both physical and chemical changes. The latter tend in principle to be rather simple kinds of reactions involving dissolution, reaction with carbon dioxide, hydrolysis, hydration, and oxidation. The difficulty in studying them and in arriving at a quantitative description is that these reactions occur very slowly and may never reach an equilibrium state. A comparison of the two rightmost columns in Table 2 on page 14 provides some illustration of the overall effect of these changes, although it must be emphasized that these are relative composition data, and thus cannot show how much of a given component has been lost. In general, sodium, calcium and magnesium seem to be lost more rapidly than potassium and silicon, while iron and aluminum decrease very slowly. Individual rates are of course dependent on the particular structural units containing the element, and also vary somewhat with grain size and condition of the surface.

Action of water

Water is undoubtedly the most important weathering agent. Not only does it act as a solvent for ionic dissolution products, but it also brings other active agents such as carbon dioxide and oxygen into intimate contact with the rock material. As water percolates into the outermost layers of the crust, it extends the zone of weathering beneath the surface; the effects of this are quite noticeable in a number of buried sedimentary materials such as Paleozoic sandstones, which tend to be depleted of all but the most resistant minerals. Dissolution, the simplest of all the weathering processes, usually results in ionic species, some of which may react with water to yield acidic or alkaline solutions. Dissolution of silica, however, results in the neutral species H_4SiO_4 . Reactions involving hydration and dehydration are very common, and since the free energy changes tend to be small, these reactions can usually take place in either direction under slightly different conditions. Thus gypsum and anhydrite are interconvertible at observable rates under common environmental conditions:



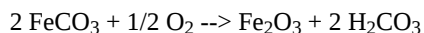
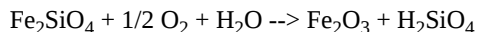
In many cases, however, the reaction products are not very well characterized, thermodynamic data is lacking, and the reactions proceed so slowly that they are not entirely understood. For example, both hydrous and anhydrous iron oxides can be found in similar geologic environments, but the little is known about the interconversion process, represented approximately as



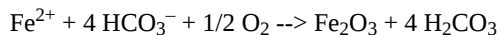
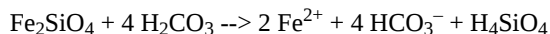
Solid carbonates tend to dissolve in acidic solutions, including those produced when atmospheric carbon dioxide dissolves in water. Thus the major surface limestone deposits (largely CaCO_3 , with some admixture of MgCO_3) tend to be highly eroded in non-arid regions, and the local groundwater may have Ca^{2+} as high as 0.1-0.2M. Thermodynamics can unambiguously predict the most stable oxidation state of a metal ion under given conditions of pH and oxidant concentration. The mechanisms tend to be very uncertain, however. For one thing, both the reactant and product can often exist in various states of hydration, and the dissolved species (which probably undergo the actual oxidation) often consist of polycations and complexed species.

Oxidation of iron

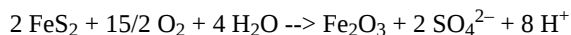
Compounds of Fe(II), for example, will always tend to oxidize to Fe(III) in the presence of air; the various oxides of iron are responsible for the bright colors seen in many geological formations, and in certain soils. Some of the net reactions that probably occur are



An environmental side effect of the first process is the release of hydrated silica. Also, where both starting materials are present, the carbonic acid produced in the second reaction is believed to promote the dissolution of ferrous silicate, creating a source of Fe(II) ions that can be rapidly oxidized:



The oxidation of sulfides can produce strongly acidic solutions:

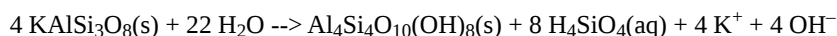


The effects of this can be seen in formations containing outcrops of pyrite veins, where the surrounding rocks are heavily stained with yellow and brown Fe(III) oxides, and the groundwater tends to be highly acidic. This process is mediated by microorganisms,

and is an important source of acid pollution associated with mines and mine tailings.

Sequence of weathering

The various components of rocks weather at different rates. The more basic components such as CaO and MgO tend to disappear first, especially if in contact with groundwaters containing high CO₂ concentrations. For rocks in general, the first reaction is usually hydration, followed by hydrolysis which can be summarized by



in which other Group 1 or 2 cations might replace potassium. The product $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ is *kaolinite*, a form of clay (see below).

In general, the rocks which crystallized first from the magma (the Ca-feldspars and olivines) weather more rapidly than do the lower-melting rocks.

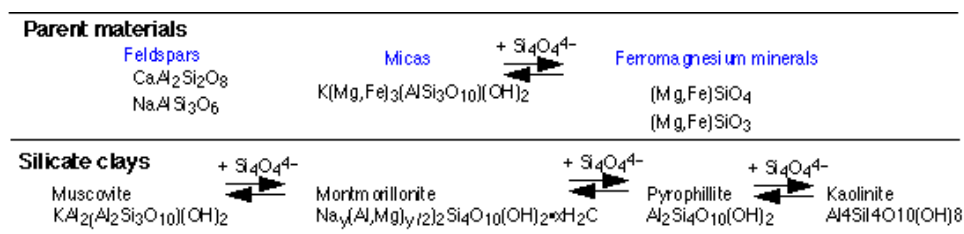


Figure 1.4.3:

Clays

Clays are the solid end products of the weathering of rocks. They are basically composed of alternating sheets of “SiO₂” and “AlO₆” units in ratios of 1:1 (kaolinite), 2:1 (montmorillonite and vermiculite) and 2:2 (chlorite). In between the sheets, and holding them together by hydrogen bonding are water molecules. Also present are cations such as K⁺, Ca²⁺ and Mg²⁺ which act to neutralize the negative charges of the oxide ions.

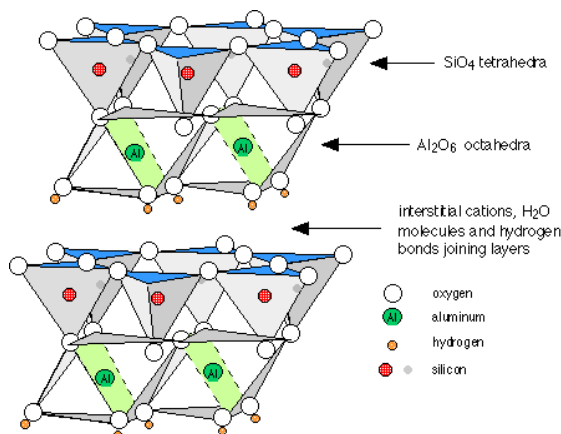


Figure 1.4.4: Structure of a clay, showing two layers of the stacked sheets of kaolinite

Physical weathering

The major agents of physical weathering of exposed rocks are rapid changes in temperature (promoting fracture by differential expansion), the abrasive action of windborne material and glacier movement, and especially by the penetration of water into cracks and its subsequent freezing. The expansion of water on freezing can exert a pressure of 150 kg cm⁻², whereas the tensile strength of a typical rock is around 120 kg cm⁻². The roots of some plants are able to penetrate rock quite effectively, producing comparable expansive pressures in subsurface rocks.

Composition and structure of soils

Soils are a product of the interaction of water, air, and living organisms with exposed rocks or sediments at the earth's surface. A typical soil contains about 45% inorganic solids and 5% organic solids by volume. Water and air each make up about 20-30%.

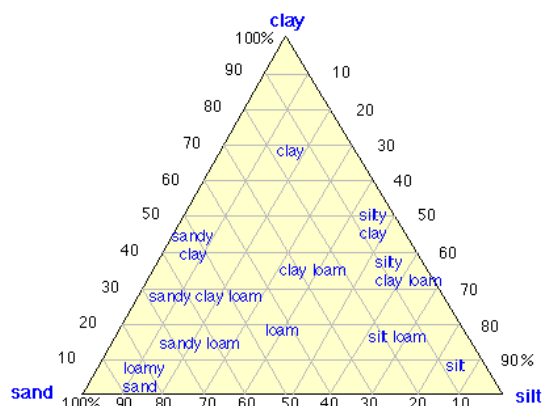


Figure 1.4.5: A simple way of classifying soils is based on the relative quantities of clay, silt and sand in the solid component. For ordinary agricultural purposes, loams are considered the most ideal soil type.

Mineral Components of soil

The primary inorganic components of soils consist of sand and silt particles that come directly from the parent rocks. This fraction is dominated by quartz and feldspars (aluminosilicates). Secondary components are formed by chemical changes within the soil itself, or in sediments from which the soil derived. These are most commonly clays, but may also include calcite, gypsum, and sulfide minerals such as pyrites; the latter are formed by bacterial action under reducing conditions in the presence of organic matter.

The clays have an especially important effect on both the physical properties of the soil, and on its ability to store plant nutrients, including trace nutrients such as Mo and Mn. These properties are due to the high ion-exchange capacity of clays. The more highly charged cations such as Al^{3+} and Fe^{3+} tend to be more strongly absorbed within the inter-sheet regions than do Mg^{2+} or K^{+} . As plants withdraw these latter cations from the soil water, more are released by the clay components, which thus act as nutrient reservoirs.

The ion-exchange properties of clays also help to maintain the pH balance of soils, through the exchange of H^{+} and cations such as Ca^{2+} . The soil pH, in turn, strongly affects the solubility of nutrient cations, and thus their availability to plants. For example, the uptake of phosphorus (in the form of $\text{H}_2\text{PO}_4^{2-}$), is only efficient within the rather narrow pH range between 6 and 7. Below 6, dihydrogen phosphates of Fe and Al are precipitated, while insoluble $\text{Ca}_3(\text{PO}_4)_2$ forms at higher pH's.

Organic Components

Part of the organic matter of soil consists of organisms (mainly bacteria and fungi) and roots and root hairs. The remainder is largely in the form of fulvic and humic acids. These substances of indefinite composition are classified on the basis of their solubility behavior; fulvic acids remain in solution at pH 2, but humic acids, having molecular weights of 20,000 to 100,000, are precipitated. Both are flexible polyelectrolytes that interact strongly with their own kind and with inorganic ions.

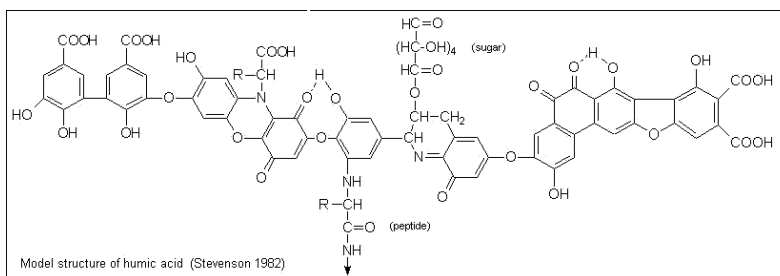


Figure 1.4.6: Model structure of humic acid (Stevenson 1982)

Associated with the fulvic and humic fractions are a wide variety smaller molecules such as alkanes, amino acids, amino sugars, sulfur and phosphorus derivatives of sugars, etc. Part of the organic carbon in a fertile soil is recycled in 1-2 years; plant residues, which are the major source of soil organic matter, have a half-life of days to months. Once carbon gets incorporated into humic substances, it is locked into a much slower recycling process; the turnover times of fulvic acids are a hundred years or more, while those for humic acids are around a thousand years. For this reason, humic substances are the major reservoir of organic carbon in soil. Organic matter, particularly polysaccharides, binds strongly to the cation components of clay colloids; the two together act as cementing agents and strongly influence the consistency and structure of the soil.

Water

Soil water is held by capillary action and adsorption with varying degrees of tenacity. This water binding strength is traditionally expressed in terms of the pressure, or “tension” that would be required to force the water out of the soil. The tension of capillary water varies over a wide range of 0.1-32 atm; only in the lower half of this range will it be available to plants, which can exert an osmotic pressure of up to about 15 atm. Water in excess of the capillary capacity fills larger voids and is called gravitational water. Its presence in surface soils corresponds to a flooded condition that inhibits plant growth by reducing soil aeration.

Air

The gas phase within soil pores generally has a CO₂ content of 5-50 times that of the atmosphere due to the action of organisms. O₂ tends to be depleted to roughly the extent that CO₂ is present in excess. Under conditions of poor aeration (i.e., exchange with the atmosphere), considerable quantities of N₂O, NO, H₂, CH₄, C₂H₄, and H₂S may also be present.

[What is soil? An introductory survey](#)

[Soils interactive textbook](#)

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O	466,000
Si	277,200
Al	81,300
Fe	50,000
Ca	36300

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CHAPTER OVERVIEW

2: The Hydrosphere

Water is the most abundant substance at the earth's surface. Almost all of it is in the oceans, which cover 70% of the surface area of the earth. However, the amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere and the oceans. Water interacts with both the atmosphere and the lithosphere, acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

[2.1: Water, Water Everywhere...](#)

[2.2: The hydrosphere and the oceans](#)

[2.3: Chemistry and geochemistry of the oceans](#)

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2.1: Water, Water Everywhere...

Water is the most abundant substance at the earth's surface. Almost all of it is in the oceans, which cover 70% of the surface area of the earth. However, the amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the [lithosphere](#) and the oceans. Water interacts with both the atmosphere and the lithosphere, acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

Reservoir	Volume / $10^6, \text{ km}^3$	Percent of total
Oceans	1370	97.25
Ice caps and glaciers	39	2.05
Deep groundwater	5.3	0.38
Shallow groundwater	4.3	0.30
Lakes	0.125	0.01
Soil moisture	0.065	0.005
Atmosphere	0.013	0.001
Rivers	0.0017	0.0001
Biosphere	0.0006	0.00004
Total	1408.7	100

Composition of Seawater

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts. As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

Table 1: Major ions of seawater: These values, expressed in parts per thousand, are for seawater of 35% salinity.

cations	g/kg	anions	g/kg
Na^+	10.77	Cl^-	19.354
Mg^{2+}	1.29	SO_4^{2-}	2.712
Ca^{2+}	0.412	Br^-	0.087
K^+	0.399		
Sr^{2+}	0.0079		
Al^{3+}	0.005		

The best way of characterizing seawater is in terms of its ionic content, shown above. The remarkable thing about seawater is the constancy of its relative ionic composition. The overall salt content, known as the salinity (grams of salts contained in 1 kg of seawater), varies slightly within the range of 32-37.5%, corresponding to a solution of about 0.7% salt content. The ratios of the concentrations of the different ions, however, are quite constant, so that a measurement of Cl^- concentration is sufficient to determine the overall composition and total salinity. Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found

in marine organisms include barium, cobalt, copper, lead, nickel, silver and zinc. Si^{32} , presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

pH balance. Reflecting this constant ionic composition is the pH, which is usually maintained in the narrow range of 7.8-8.2, compared with 1.5 to 11 for fresh water. The major buffering action derives from the carbonate system, although ion exchange between Na^+ in the water and H^+ in clay sediments has recently been recognized to be a significant factor.

Conservative and non-conservative substances

The major ionic constituents whose concentrations can be determined from the salinity are known as conservative substances. Their constant relative concentrations are due to the large amounts of these species in the oceans in comparison to their small inputs from river flow. This is another way of saying that their residence times are very large.

Table 2: Replacement time with respect to river addition for some components of seawater. Concentrations in micromols/L

component	concentration in river water	concentration in seawater	residence time, 10^6 y
Cl^-	250	558,000	87
Na^+	315	479,000	55
Mg^{2+}	150	54,300	13
SO_4^{2-}	120	28,900	8.7
Ca^{2+}	367	10,500	1
K^+	36	10,400	10
HCO_3^-	870	2000	0.083
H_4SiO_4	170	100	0.021
NO_3^-	10	20	0.072
H_2PO_4^-	0.7	1	0.080

A number of other species, mostly connected with biological activity, are subject to wide variations in concentration. These include the nutrients NO_3^- , NO_2^- , NH_4^+ , and HPO_4^{2-} , which may become depleted near the surface in regions of warmth and light. As was explained in the preceding subsection on coastal upwelling, offshore prevailing winds tend to drive Western coastal surface waters out to sea, causing deeper and more nutrient-rich water to be drawn to the surface. This upwelled water can support a large population of phytoplankton and thus of zooplankton and fish. The best-known example of this is the anchovy fishery off the coast of Peru, but the phenomenon occurs to some extent on the West coasts of most continents, including our own.

Other non-conservative components include Ca^{2+} and SiO_4^{2-} . These ions are incorporated into the solid parts of marine organisms, which sink to greater depths after the organisms die. The silica gradually dissolves, since the water is everywhere undersaturated in this substance. Calcium carbonate dissolves at intermediate depths, but may reprecipitate in deep waters owing to the higher pressure. Thus the concentrations of Ca and of SiO_4^{2-} tend to vary with depth. The gases O_2 and CO_2 , being intimately involved with biological activity, are also non-conservative, as are N_2O and CO.

Organic matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as "Gelbstoffe". It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly

covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

Regulation of ocean composition

The salinity of the ocean appears to have been about the same for at least the last 200 million years. There have been changes in the relative amounts of some species, however; the ratio of Na/K has increased from about 1:1 in ancient ocean sediments to its present value of 28:1. Incorporation of calcium into sediments by the action of marine organisms has depleted the Ca/Mg ratio from 1:1 to 1:3.

Table: Mass balance of P, C, and Ca for the oceans

element	input to ocean	dissolved in seawater	in dead organisms	loss to sediments	residence time, y
phosphorus	1 (erosion)	1	1	1 (organic)	10,000
carbon	100 as CO ₂ 500 as carbonate	1000	125	100 (organic) 600 (carbonate)	165,000
calcium	500 (erosion)	5000	25	500 (as CaCO ₃)	10 ⁶

If the composition of the ocean has remained relatively unchanged with time, the continual addition of new mineral substances by the rivers and other sources must be exactly balanced by their removal as sediment, possibly passing through one or more biological systems in the process.

Where does the Salt Come From?

In 1715 Edmund Halley suggested that the age of the ocean (and thus presumably of the world) might be estimated from the rate of salt transport by rivers. When this measurement was actually carried out in 1899, it gave an age of only 90 million years.

This is somewhat better than the calculation made in 1654 by James Ussher, the Anglican Archbishop of Armagh, Ireland, based on his interpretation of the Biblical book of Genesis, that the world was created at 9 A.M. on October 23, 4004 BC, but it is still far too recent, being about when the dinosaurs became extinct. What Halley actually described was the residence time, which is about right for Na but much too long for some of the minor elements of seawater.

The commonly stated view that the salt content of the oceans derives from surface runoff that contains the products of weathering and soil leaching is not consistent with the known compositions of the major river waters (See Table). The halide ions are particularly over-represented in seawater, compared to fresh water. These were once referred to as “excess volatiles”, and were attributed to volcanic emissions. With the discovery of plate tectonics, it became apparent that the locations of seafloor spreading at which fresh basalt flows up into the ocean from the mantle are also sources of mineral-laden water. Some of this may be seawater that has cycled through a hot porous region and has been able to dissolve some of the mineral material owing to the high temperature. Much of the water, however, is “juvenile” water that was previously incorporated into the mantle material and has never before been in the liquid phase. The substances introduced by this means (and by volcanic activity) are just the elements that are “missing” from river waters. Estimates of what fraction of the total volume of the oceans is due to juvenile water (most of it added in the early stages of mantle differentiation that began a billion years ago) range from 30 to 90%.

Geochemical processes involving the oceans

The oceans can be regarded as a product of a giant acid-base titration in which the carbonic acid present in rain reacts with the basic materials of the lithosphere. The juvenile water introduced at locations of ocean-floor spreading is also acidic, and is partly neutralized by the basic components of the basalt with which it reacts. Surface rocks mostly contain aluminum, silicon and oxygen combined with alkali and alkaline-earth metals, mainly potassium, sodium and calcium. The CO₂ and volcanic gases in rainwater react with this material to form a solution of the metal ion and HCO₃⁻, in which is suspended some hydrated SiO₂. The solid material left behind is a clay such as kaolinite, Al₂Si₂O₅(OH)₄. This first forms as a friable coating on the surface of the weathered

rock; later it becomes a soil material, then an alluvial deposit, and finally it may reach the sea as a suspended sediment. Here it may undergo a number of poorly-understood transformations to other clay sediments such as illites. Sea floor spreading eventually transports these sediments to a subduction region under a continental block, where the high temperatures and pressures permit reactions that transform it into hard rock such as granite, thus completing the geochemical cycle.

Deep-sea hydrothermal vents are now recognized to be another significant route for both the addition and removal of ionic substances from seawater.

Distribution and cycling of elements in the oceans

Although the relative concentrations of most of the elements in seawater are constant throughout the oceans, there are certain elements that tend to have highly uneven distributions vertically, and to a lesser extent horizontally. Neglecting the highly localized effects of undersea springs and volcanic vents, these variations are direct results of the removal of these elements from seawater by organisms; if the sea were sterile, its chemical composition would be almost uniform.

Plant life can exist only in the upper part of the ocean where there is sufficient light available to drive photosynthesis. These plants, together with the animals that consume them, extract nutrients from the water, reducing the concentrations of certain elements in the upper part of the sea. When these organisms die, they fall toward the lower depths of the ocean as particulate material. On the way down, some of the softer particles, deriving from tissue, may be consumed by other animals and recycled. Eventually, however, the nutrient elements that were incorporated into organisms in the upper part of the ocean will end up in the colder, dark, and essentially lifeless lower part.

Mixing between the upper and lower reservoirs of the ocean is quite slow, owing to the higher density of the colder water; the average residence time of a water molecule in the lower reservoir is about 1600 years. Since the volume of the upper reservoir is only about 1/20 of that of the lower, a water molecule stays in the upper reservoir for only about 80 years.

Except for dissolved oxygen, all elements required by living organisms are depleted in the upper part of the ocean with respect to the lower part. In the case of the major nutrients P, N and Si, the degree of depletion is sufficiently complete (around 95%) to limit the growth of organisms at the surface. These three elements are said to be biolimiting. A few other biointermediate elements show partial depletion in surface waters: Ca (1%), C (15%), Ba (75%).

The organic component of plants and animals has the average composition $C_{80}N_{15}P$. It is remarkable that the ratio of N:P in seawater (both surface and deep) is also 15:1; this raises the interesting question of to what extent the ocean and life have co-evolved.

In the deep part of the ocean the elemental ratio corresponds to $C_{800}N_{15}P$, but of course with much larger absolute amounts of these elements. Eventually some of this deeper water returns to the surface where the N and P are quickly taken up by plants. But since plants can only utilize 80 out of every 800 carbon atoms, 90 percent of the carbon will remain in dissolved form, mostly as HCO_3^- .

To work out the balance of Ca and Si used in the hard parts of organisms, we add these elements to the average composition of the lower reservoir to get $Ca_{3200}Si_{50}C_{800}N_{15}P$. Particulate carbon falls into the deep ocean in the ratio of about two atoms in organic tissue to one atom in the form of calcite. This makes the overall composition of detrital material something like $C_{120}N_{15}P$; i.e., 80 organic C's and 40 in $CaCO_3$. Accompanying these 40 calcite units will be 40 Ca atoms, but this represents a minor depletion of the 3200 Ca atoms that eventually return to the surface, so this element is only slightly depleted in the upper waters. Silicon, being far less abundant, is depleted to a much greater extent.

The oceanic sediments

The particulate shower

A continual rain of particulate material from dead organisms falls through the ocean. This shower is comprised of three major kinds of material: calcite ($CaCO_3$), silica (SiO_2), and organic matter. The first two come from the hard parts of both plants and animals (mainly microscopic animals such as foraminifera and radiolarians). The organic matter is derived mainly from the soft tissues of

organisms, and from animal fecal material. Some of this solid material dissolves before it reaches the ocean floor, but not usually before it enters the deep ocean where it will remain for about 1600 years.

The remainder of this material settles onto the floor of the sea, where it forms one component of a layer of sediments that provide important information about the evolution of the sea and of the earth. Over a short time scale of months to years, these sediments are in quasi-equilibrium with the seawater. On a scale of millions of years, the sediments are merely way-stations in the geochemical cycling of material between the earth's surface and its interior.

The oceanic sediments have three main origins:

- **Detrital** material is derived largely from particles deposited in the ocean by rivers and also directly by the wind. These materials are mostly aluminosilicates (clays), along with some quartz. These substances accumulate on the deep ocean floor at a rate of about 0.3 g cm^{-2} per 1000 years.
- **Authigenic** materials are formed by precipitation within the ocean or by crystallization within the sediment itself. These constitute only a small fraction of the total sediment.
- **Biogenic** components consist mainly of the calcium carbonate and silica that make up the hard parts of organisms. Scavenging by other organisms is so efficient that only about 0.3 % of the total deep sea sediment consists of actual organic material.

Our main interest lies with the silica and calcium carbonate, since these substances form a crucial part of the biogeological cycle. Also, their distributions in the ocean are not uniform- a fact that must tell us something.

The skeletons of diatoms and radiolarians are the principal sources of silica sediments. Since the ocean is everywhere undersaturated with respect to silica, only the most resistant parts of these skeletons reach the bottom of the deep ocean and get incorporated into sediments. Silica sediments are less common in the Atlantic ocean, owing to the lower content of dissolved silica.

The parts of the ocean where these sediments are increasing most rapidly correspond to regions of upwelling, where deep water that is rich in dissolved silica rises to the surface where the silica is rapidly fixed by organisms. Where upwelling is absent, the growth of the organisms is limited, and little silica is precipitated. Since deep waters tend to flow from the Atlantic into the Pacific ocean where most of the upwelling occurs, Atlantic waters are depleted in silica, and silica sediments are not commonly found in this ocean.

For calcium carbonate, the situation is quite different. In the first place, surface waters are everywhere supersaturated with respect to both calcite and aragonite, the two common crystal forms of CaCO_3 . Secondly, Ca^{2+} and HCO_3^- are never limiting factors in the growth of the coccoliths (plants) and forams (animals) that precipitate CaCO_3 ; their production depends on the availability of phosphate and nitrogen. Because these elements are efficiently recycled before they fall into the deep ocean, their supply does not depend on upwelling, and so the production of solid is more uniformly distributed over the world's oceans.

More importantly, however, the chances that a piece of carbonate skeleton will end up as sediment will be highly dependent on both the local CO_3^{2-} concentration and the depth of the ocean floor. These factors give rise to small-scale variations in the production of carbonate sediments that can be quite wide-ranging.

Ocean sediments and continental drift

New crust is being generated and moving away from the crests of the mid-ocean ridges at a rate of a few centimetres per year. Although the crests of these ridges are relatively high points, projecting to within about 3000 m of the surface, the continual injection of new material prevents sediments from accumulating in these areas. Farther from the crests, carbonate sediments do build up, eventually reaching a depth of about 500 m, but by this time the elevation has dropped off below the saturation horizon, so from this point on the carbonate sediments are overlaid by red clay.

If we drill a hole down through a part of the ocean floor that is presently below the saturation horizon, the top part of the drill core will consist of clay, followed by CaCO_3 at greater depths. The core may also contain regions in which silica predominates. Since silica production is very high in equatorial regions, the appearance of such a layer suggests that this particular region of the oceanic crust has moved across the equator.

Contributors and Attributions

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2.2: The hydrosphere and the oceans

*How inappropriate to call this planet Earth,
when clearly it is Ocean."*

Arthur C. Clarke

Water is the most abundant substance at the earth's surface. Almost all of it is in the oceans, which cover 70% of the surface area of the earth. However, the amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere and the oceans.

Water interacts with both the atmosphere and the lithosphere, acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

Table2.2.1: Inventory of water on Earth

Reservoir	Volume / $10^6, \text{km}^3$	Percent of total
Oceans	1370	97.25
Ice caps and glaciers	39	2.05
Deep groundwater	5.3	0.38
Shallow groundwater	4.3	0.30
Lakes	0.125	0.01
Soil moisture	0.065	0.005
Atmosphere	0.013	0.001
Rivers	0.0017	0.0001
Biosphere	0.0006	0.00004
Total	1408.7	100

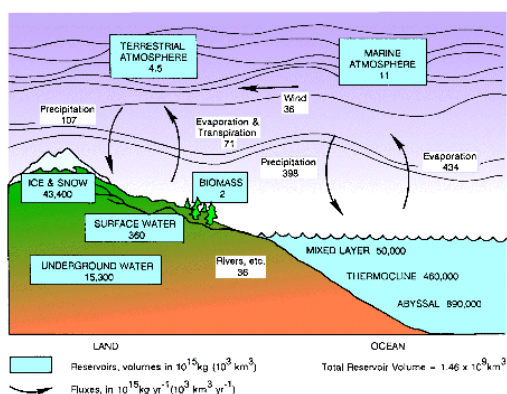
Where did the water come from?

It appears to have been bound up in the silica-based materials such as micas and amphiboles which accreted to form the Earth. The heat released during this process would have been sufficient to drive off this water, which amounted to about 0.01% by mass of the primordial material.

The hydrologic cycle

The *hydrologic cycle* refers to the steady state that exists between evaporation, condensation, percolation, runoff, and circulation of water. The cycle is driven by solar energy, mainly through direct vaporization, but also by convective motion induced by uneven heating.

The major interphase transport process of the hydrologic cycle is evaporation of water from the ocean. However, 90% of this vapor falls directly back into the ocean as rain, while 10% is transported over the land. Of the latter, about two-thirds evaporates again and one third runs off to the ocean.



The climatic hydrologic cycle at global scale [from NRC, 1986].

Figure 2.2.1: The climatic hydrological cycle at global scale (Diagram and text from a [page](#) at the [Web site](#) of the Institute for Global Environment and Society)

The movement of water on the earth's surface and through the atmosphere is known as the hydrologic cycle. Water is taken up by the atmosphere from the earth's surface in vapor form through evaporation. It may then be moved from place to place by the wind until it is condensed back to its liquid phase to form clouds. Water then returns to the

surface of the earth in the form of either liquid (rain) or solid (snow, sleet, etc.) precipitation. Water transport can also take place on or below the earth's surface by flowing glaciers, rivers, and ground water flow.

The amounts of water precipitated onto the land and oceans are in approximate proportion to the relative surface areas, but evaporation from the ocean exceeds that from the land by about $37,400 \text{ km}^3 \text{ yr}^{-1}$. This difference is the amount of water transported to the oceans by river runoff. When water condenses from the atmosphere in the form of rain, it is slightly enriched in H_2O^{18} . During epochs of glacial buildup the fraction of H_2O^{18} in the oceans consequently decreases. Observation of $\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16}$ ratios in marine sediments is one way of studying the timing and extent of past glaciations. Since the degree of heavy isotope enrichment of condensed water is temperature dependent, this same method can be used to estimate mean world temperatures in the distant past.

The hydrologic cycle also has important effects on the energy budget of the earth. Atmospheric water vapor (along with carbon dioxide and methane) tends to absorb the long-wavelength infrared radiation emitted by the earth's surface, partially trapping the incoming shorter-wavelength energy and thus maintaining the mean surface temperature about 30° higher than would be the case in the absence of water vapor. Of the 51% of the solar radiation incident on the atmosphere that reaches the earth's surface, about half of this (23%) is used to evaporate water. During the ten days that an average molecule resides in the atmosphere, it will travel about 1000 km. The atmospheric transport of water from equatorial to subtropical regions serves as an important mechanism for the transport of thermal energy; at latitudes of about 40° , as much as one-third of the energy input comes from release of latent heat from water vapor formed in equatorial regions.

Oceanic circulation

About 97% of the earth's water is contained in the two reservoirs which comprise the oceans. The upper mixed layer contains about 5% of the total; it is separated from the deeper and colder layer by the thermocline. Mixing between these two stratified layers is very slow; of the total ocean volume of $6.8 \times 10^{18} \text{ m}^3$, only about $0.71 \times 10^{15} \text{ m}^3$, or about 0.01%, moves between the two layers per year. The mean residence time of a water molecule in the deep layer is about 1600 years.

The large-scale motions of ocean water are the primary means by which chemical substances, especially those taken up and excreted by organisms, are transported within the ocean. An understanding of the general patterns of this circulation is essential in order to analyze the observed distribution of many of the chemical elements in different parts of the ocean and in the oceanic sediments.

Atmospheric circulation

The circulation of the surface waters of the ocean is driven by the prevailing winds. The latter arise from uneven heating of the earth's surface, and are arranged in bands that parallel the equator.

Although the motion of the waters at the surface of the ocean are driven by the winds, they do not follow them in a simple manner. The reasons are threefold: the Coriolis effect, the presence of land masses, and unevenness in the sea level due to regional differences in temperature and atmospheric pressure.

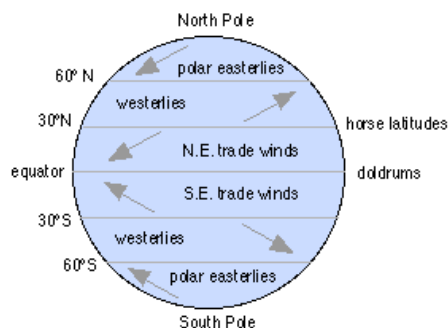


Figure 2.2.2: Atmospheric winds

The most intense heat input into the atmosphere occurs near the equator, where the heated air rises and cools, producing intense local precipitation but little surface wind. After cooling and losing moisture, this air moves north and south and descends at a latitude of about 30° . As it descends, it warms (largely by adiabatic compression) and its relative humidity decreases. The extreme dryness of this air gives rise to the subtropical desert regions between about 15° and 30° . Part of this air flows back toward the equator, giving rise to the northeast and southwest trade winds; the deflection to the east or west is caused by the Coriolis effect. Another part of the descending air travels poleward, producing the prevailing westerlies. Eventually these collide with cold air masses moving away from the polar regions, producing a region of unstable air and storm activity known as a polar front. Some of this polar air picks up enough heat to rise and enter into polar cell circulation patterns.

The flow of air in the prevailing westerlies is subject to considerable turbulence which gives rise to planetary waves. These are moving regions in which warm surface air is lifted to higher levels, producing lines of storms that travel from west to east, and exchanging more air between the polar and temperate regions.

Surface currents of the oceans

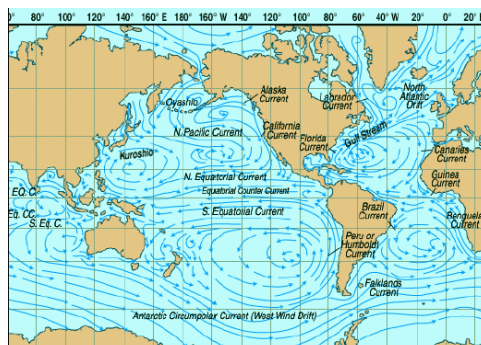


Figure 2.2.3:

In the Northern hemisphere, the Coriolis effect not only deflects south-moving objects to the east but it also causes currents flowing parallel to the equator to veer to the right of the direction of flow, i.e. to the north or south.

In addition, prevailing westerly winds and the eastward rotation of the earth cause water to pile up by a few centimeters at the western edges of the oceans. The resultant downhill flow, interacting with Coriolis forces, produces a *western boundary current* that runs south-to-north in the northern hemisphere. A similar but opposite effect gives rise to a south-flowing *eastern boundary current* on continental east coasts.

Thermohaline circulation

In contrast to the upper levels of the ocean, the deep ocean is *stratified*; the density increases with depth so as to inhibit the vertical transport of water. This stratification divides the deep oceans into several distinct water masses which undergo movement in a more or less horizontal plane, with adjacent masses sometimes moving in opposite directions.

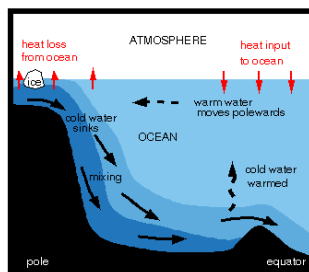


Figure 2.2.4: As the cold water fills up the deepest regions and spills over ridges into other deep basins, it creates huge undersea cascades which rival the greatest terrestrial waterfalls in height and the largest rivers in volume. For more on this, see the Feb. 1989 *Scientific American*

The winds and atmospheric effects outlined above affect only the upper part of the ocean. Below 100 meters or so, oceanic circulation is driven by the *density* of the seawater, which is determined by its temperature and its salinity. Variations in these two quantities give rise to the *thermohaline circulation* of the deep currents of the ocean. It all starts when seasonal ice begins to form in the polar regions. Because the salts dissolved in seawater cannot be accommodated within the ice structure, they are largely excluded from the new ice and remain in solution. This increases the density of the surrounding unfrozen water, causing it to sink into the bottom ocean.

There are two major locations at which surface waters enter the deep ocean. The northern entry point is in the Norwegian Sea off Greenland; this water forms a mass known as the North Atlantic Deep Water (NADW) which flows southward across the equator.

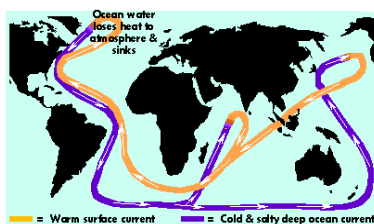
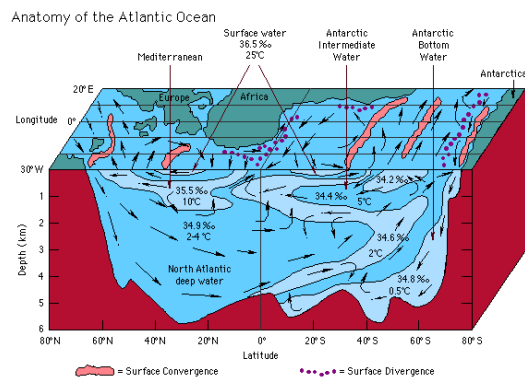


Figure 2.2.5: From Don Reed, *Marine Geology 130* at San Jose State U.

Most of the transport into the deep ocean takes place in the Weddell Sea off the coast of Antarctica. The highly saline water flows down the submerged Antarctic Slope to begin a 5000-year trip to the north across the bottom of the ocean. This is the major route by which dissolved CO_2 and O_2 (which are more soluble in this cold water) are transported into the deep ocean where it forms a water mass known as the Antarctic Bottom Water (AABW) which can be traced into all three oceans.

In the south, a flow from the antarctic region forms a water mass known as the Antarctic Bottom Water (AABW) which can be traced into all three oceans.

The Pacific Ocean lacks any major identifiable direct source of cold water, so it is less differentiated and its deep circulation is sluggish and poorly defined.



Adapted from Duxbury, Allyn C. and Allison B. Duxbury. *An Introduction to the World's Oceans*. 1994. Wm. C. Brown Publishers.

Figure 2.2.6: Temperature and salinity profiles in a north-south subsection of the Atlantic ocean.

As is apparent from the figure above, the vertical profiles of temperature and especially of the salinity are not uniform. To some extent, these two parameters have opposite effects: in equatorial regions, temperatures are higher (leading to lower density) but evaporation rates are also higher (leading to higher density). In polar regions, the formation of sea ice raises the density of the seawater (because only a small proportion of salt is incorporated into the ice).

The nature and extent of the deep ocean currents differ in the Atlantic, Pacific, and Indian oceans. These currents are much slower than the surface currents, and in fact have not been measured directly; their existence is however clearly implied by the chemical composition and temperature of water samples taken from various parts of the ocean. Estimated rates are of the order of kilometers per month, in contrast to the few kilometers per hour of surface waters. The deep currents are the indirect results of processes occurring at the surface in which cold water of high salinity is produced as sea ice forms in the arctic and antarctic regions. This water is so dense that it sinks to the bottom, displacing warmer or less saline water as it moves.

Coastal Upwelling

Recirculation of deep water to the surface occurs to a very small extent in many regions, but it is especially pronounced where water entering the Antarctic Bottom mass displaces other bottom water, and where water piles up at the western edges of continents. This latter water flows downhill (forming the western boundary currents mentioned above) and is replaced by colder water from the deep ocean. The deep ocean contains few organisms to deplete the water of the nutrients it receives from the remains of the dead organisms floating down from above; this upwelled water is therefore exceptionally rich in nutrients, and strongly encourages the growth of new organisms that extend up the food chain to fish. Thus the wind-driven upwelling that occurs off the west coast of South America is responsible for the Peruvian fishing and guano fertilizer industry.

About every seven years these prevailing winds disappear for a while, allowing warm equatorial waters to move in. This phenomenon is known as El Niño and it results in massive kills of plankton and fish. Decomposition of the dead organisms reduces the oxygen content of the water, causing the death of still more fish, and allowing reduced compounds such as hydrogen sulfide to accumulate.

Matthias Tomczak's [Introduction to physical oceanography](#) is an excellent source of more information on the topics covered above.

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2.3: Chemistry and geochemistry of the oceans

Composition of seawater

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts.

As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

		cations	g/kg	anions	g/kg
Major ions of seawater These values, expressed in parts per thousand, are for seawater of 35‰ salinity.		Na ⁺	10.77	Cl ⁻	19.354
		Mg ²⁺	1.29	SO ₄ ²⁻	2.712
		Ca ²⁺	0.412	Br ⁻	0.087
		K ⁺	0.399		
		Sr ²⁺	0.0079		
		Al ³⁺	0.005		

The best way of characterizing seawater is in terms of its ionic content, shown above. The remarkable thing about seawater is the constancy of its relative ionic composition. The overall salt content, known as the salinity (grams of salts contained in 1 kg of seawater), varies slightly within the range of 32-37.5‰, corresponding to a solution of about 0.7% salt content. The ratios of the concentrations of the different ions, however, are quite constant, so that a measurement of Cl⁻ concentration is sufficient to determine the overall composition and total salinity. Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found in marine organisms include barium, cobalt, copper, lead, nickel, silver and zinc. Si³², presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

pH balance. Reflecting this constant ionic composition is the pH, which is usually maintained in the narrow range of 7.8-8.2, compared with 1.5 to 11 for fresh water. The major buffering action derives from the carbonate system, although ion exchange between Na⁺ in the water and H⁺ in clay sediments has recently been recognized to be a significant factor.

Conservative and non-conservative substances

The major ionic constituents whose concentrations can be determined from the salinity are known as conservative substances. Their constant relative concentrations are due to the large amounts of these species in the oceans in comparison to their small inputs from river flow. This is another way of saying that their residence times are very large.

Ion	Concentration in river water micromols/L	Concentration in sea water micromols/L	Residence time/10 ⁶ years
Cl ⁻	250	558,000	87
Na ⁺	315	479,000	55
Mg ²⁺	150	54,300	13
SO ₄ ²⁻	120	28,900	8.7
Ca ²⁺	367	10,500	1
K ⁺	36	10,400	10
HCO ₃ ⁻	870	2000	0.083

Ion	Concentration in river water micromols/L	Concentration in sea water micromols/L	Residence time/ 10^6 years
H ₄ SiO ₄	170	100	0.021
NO ₃ [−]	10	20	0.072
H ₂ PO ₄ [−]	0.7	1	0.080

Replacement time with respect to river addition for some components of seawater

A number of other species, mostly connected with biological activity, are subject to wide variations in concentration. These include the nutrients NO_3^- , NO_2^- , NH_4^+ , and HPO_4^{2-} , which may become depleted near the surface in regions of warmth and light. As was explained in the preceding subsection on coastal upwelling, offshore prevailing winds tend to drive Western coastal surface waters out to sea, causing deeper and more nutrient-rich water to be drawn to the surface. This upwelled water can support a large population of phytoplankton and thus of zooplankton and fish. The best-known example of this is the anchovy fishery off the coast of Peru, but the phenomenon occurs to some extent on the West coasts of most continents, including our own.

Other non-conservative components include Ca^{2+} and SiO_4^{2-} . These ions are incorporated into the solid parts of marine organisms, which sink to greater depths after the organisms die. The silica gradually dissolves, since the water is everywhere undersaturated in this substance. Calcium carbonate dissolves at intermediate depths, but may reprecipitate in deep waters owing to the higher pressure. Thus the concentrations of Ca and of SiO_4^{2-} tend to vary with depth. The gases O_2 and CO_2 , being intimately involved with biological activity, are also non-conservative, as are N_2O and CO .

Organic matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as "*Gelbstoffe*". It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

Regulation of ocean composition

The salinity of the ocean appears to have been about the same for at least the last 200 million years. There have been changes in the relative amounts of some species, however; the ratio of Na/K has increased from about 1:1 in ancient ocean sediments to its present value of 28:1. Incorporation of calcium into sediments by the action of marine organisms has depleted the Ca/Mg ratio from 1:1 to 1:3.

Mass balance of P, C, and Ca for the oceans

Element	input to ocean	dissolved in seawater	in dead organisms	loss to sediments	residence time, y
phosphorus	1 (erosion)	1	1	1 (organic)	10,000
carbon	100 as CO_2 500 as carbonate	1000	125	100 (organic) 600 (carbonate)	165,000
calcium	500 (erosion)	5000	25	500 (as CaCO_3)	10^6

If the composition of the ocean has remained relatively unchanged with time, the continual addition of new mineral substances by the rivers and other sources must be exactly balanced by their removal as sediment, possibly passing through one or more biological systems in the process.

Where does the salt come from?

In 1715 Edmund Halley suggested that the age of the ocean (and thus presumably of the world) might be estimated from the rate of salt transport by rivers. When this measurement was actually carried out in 1899, it gave an age of only 90 million years.

This is somewhat better than the calculation made in 1654 by James Ussher, the Anglican Archbishop of Armagh, Ireland, based on his interpretation of the Biblical book of Genesis, that the world was created at 9 A.M. on October 23, 4004 BC, but it is still far too recent, being about when the dinosaurs became extinct. What Halley actually described was the residence time, which is about right for Na but much too long for some of the minor elements of seawater.

The commonly stated view that the salt content of the oceans derives from surface runoff that contains the products of weathering and soil leaching is not consistent with the known compositions of the major river waters (See Table). The halide ions are particularly over-represented in seawater, compared to fresh water. These were once referred to as “excess volatiles”, and were attributed to volcanic emissions. With the discovery of plate tectonics, it became apparent that the locations of seafloor spreading at which fresh basalt flows up into the ocean from the mantle are also sources of mineral-laden water. Some of this may be seawater that has cycled through a hot porous region and has been able to dissolve some of the mineral material owing to the high temperature. Much of the water, however, is “juvenile” water that was previously incorporated into the mantle material and has never before been in the liquid phase. The substances introduced by this means (and by volcanic activity) are just the elements that are “missing” from river waters. Estimates of what fraction of the total volume of the oceans is due to juvenile water (most of it added in the early stages of mantle differentiation that began a billion years ago) range from 30 to 90%.

Geochemical processes involving the oceans

The oceans can be regarded as a product of a giant acid-base titration in which the carbonic acid present in rain reacts with the basic materials of the lithosphere. The juvenile water introduced at locations of ocean-floor spreading is also acidic, and is partly neutralized by the basic components of the basalt with which it reacts. Surface rocks mostly contain aluminum, silicon and oxygen combined with alkali and alkaline-earth metals, mainly potassium, sodium and calcium. The CO_2 and volcanic gases in rainwater react with this material to form a solution of the metal ion and HCO_3^- , in which is suspended some hydrated SiO_2 . The solid material left behind is a clay such as kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. This first forms as a friable coating on the surface of the weathered rock; later it becomes a soil material, then an alluvial deposit, and finally it may reach the sea as a suspended sediment. Here it may undergo a number of poorly-understood transformations to other clay sediments such as illites. Sea floor spreading eventually transports these sediments to a subduction region under a continental block, where the high temperatures and pressures permit reactions that transform it into hard rock such as granite, thus completing the geochemical cycle.

Deep-sea hydrothermal vents are now recognized to be another significant route for both the addition and removal of ionic substances from seawater.

Distribution and cycling of elements in the oceans

Although the relative concentrations of most of the elements in seawater are constant throughout the oceans, there are certain elements that tend to have highly uneven distributions vertically, and to a lesser extent horizontally. Neglecting the highly localized effects of undersea springs and volcanic vents, these variations are direct results of the removal of these elements from seawater by organisms; if the sea were sterile, its chemical composition would be almost uniform.

Plant life can exist only in the upper part of the ocean where there is sufficient light available to drive photosynthesis. These plants, together with the animals that consume them, extract nutrients from the water, reducing the concentrations of certain elements in the upper part of the sea. When these organisms die, they fall toward the lower depths of the ocean as particulate material. On the way down, some of the softer particles, deriving from tissue, may be consumed by other animals and recycled. Eventually,

however, the nutrient elements that were incorporated into organisms in the upper part of the ocean will end up in the colder, dark, and essentially lifeless lower part.

Mixing between the upper and lower reservoirs of the ocean is quite slow, owing to the higher density of the colder water; the average residence time of a water molecule in the lower reservoir is about 1600 years. Since the volume of the upper reservoir is only about 1/20 of that of the lower, a water molecule stays in the upper reservoir for only about 80 years.

Except for dissolved oxygen, all elements required by living organisms are depleted in the upper part of the ocean with respect to the lower part. In the case of the major nutrients P, N and Si, the degree of depletion is sufficiently complete (around 95%) to limit the growth of organisms at the surface. These three elements are said to be biolimiting. A few other biointermediate elements show partial depletion in surface waters: Ca (1%), C (15%), Ba (75%).

The organic component of plants and animals has the average composition $C_{80}N_{15}P$. It is remarkable that the ratio of N:P in seawater (both surface and deep) is also 15:1; this raises the interesting question of to what extent the ocean and life have co-evolved.

In the deep part of the ocean the elemental ratio corresponds to $C_{800}N_{15}P$, but of course with much larger absolute amounts of these elements. Eventually some of this deeper water returns to the surface where the N and P are quickly taken up by plants. But since plants can only utilize 80 out of every 800 carbon atoms, 90 percent of the carbon will remain in dissolved form, mostly as HCO_3^- .

To work out the balance of Ca and Si used in the hard parts of organisms, we add these elements to the average composition of the lower reservoir to get $Ca_{3200}Si_{50}C_{800}N_{15}P$. Particulate carbon falls into the deep ocean in the ratio of about two atoms in organic tissue to one atom in the form of calcite. This makes the overall composition of detrital material something like $C_{120}N_{15}P$; i.e., 80 organic C's and 40 in $CaCO_3$. Accompanying these 40 calcite units will be 40 Ca atoms, but this represents a minor depletion of the 3200 Ca atoms that eventually return to the surface, so this element is only slightly depleted in the upper waters. Silicon, being far less abundant, is depleted to a much greater extent.

The oceanic sediments

The particulate shower.

A continual rain of particulate material from dead organisms falls through the ocean. This shower is comprised of three major kinds of material: calcite ($CaCO_3$), silica (SiO_2), and organic matter. The first two come from the hard parts of both plants and animals (mainly microscopic animals such as foraminifera and radiolarians). The organic matter is derived mainly from the soft tissues of organisms, and from animal fecal material. Some of this solid material dissolves before it reaches the ocean floor, but not usually before it enters the deep ocean where it will remain for about 1600 years.

The remainder of this material settles onto the floor of the sea, where it forms one component of a layer of sediments that provide important information about the evolution of the sea and of the earth. Over a short time scale of months to years, these sediments are in quasi-equilibrium with the seawater. On a scale of millions of years, the sediments are merely way-stations in the geochemical cycling of material between the earth's surface and its interior.

The oceanic sediments have three main origins:

- **Detrital** material is derived largely from particles deposited in the ocean by rivers and also directly by the wind. These materials are mostly aluminosilicates (clays), along with some quartz. These substances accumulate on the deep ocean floor at a rate of about 0.3 g cm^{-2} per 1000 years.
- **Authigenic** materials are formed by precipitation within the ocean or by crystallization within the sediment itself. These constitute only a small fraction of the total sediment.
- **Biogenic** components consist mainly of the calcium carbonate and silica that make up the hard parts of organisms. Scavenging by other organisms is so efficient that only about 0.3 % of the total deep sea sediment consists of actual organic material.

Our main interest lies with the silica and calcium carbonate, since these substances form a crucial part of the biogeological cycle. Also, their distributions in the ocean are not uniform- a fact that must tell us something.

The skeletons of diatoms and radiolarians are the principal sources of silica sediments. Since the ocean is everywhere undersaturated with respect to silica, only the most resistant parts of these skeletons reach the bottom of the deep ocean and get incorporated into sediments. Silica sediments are less common in the Atlantic ocean, owing to the lower content of dissolved silica.

The parts of the ocean where these sediments are increasing most rapidly correspond to regions of upwelling, where deep water that is rich in dissolved silica rises to the surface where the silica is rapidly fixed by organisms. Where upwelling is absent, the growth of the organisms is limited, and little silica is precipitated. Since deep waters tend to flow from the Atlantic into the Pacific ocean where most of the upwelling occurs, Atlantic waters are depleted in silica, and silica sediments are not commonly found in this ocean.

For calcium carbonate, the situation is quite different. In the first place, surface waters are everywhere supersaturated with respect to both calcite and aragonite, the two common crystal forms of CaCO_3 . Secondly, Ca^{2+} and HCO_3^- are never limiting factors in the growth of the coccoliths (plants) and forams (animals) that precipitate CaCO_3 ; their production depends on the availability of phosphate and nitrogen. Because these elements are efficiently recycled before they fall into the deep ocean, their supply does not depend on upwelling, and so the production of solid is more uniformly distributed over the world's oceans.

More importantly, however, the chances that a piece of carbonate skeleton will end up as sediment will be highly dependent on both the local CO_3^{2-} concentration and the depth of the ocean floor. These factors give rise to small-scale variations in the production of carbonate sediments that can be quite wide-ranging.

Ocean sediments and continental drift

New crust is being generated and moving away from the crests of the mid-ocean ridges at a rate of a few centimetres per year. Although the crests of these ridges are relatively high points, projecting to within about 3000 m of the surface, the continual injection of new material prevents sediments from accumulating in these areas. Farther from the crests, carbonate sediments do build up, eventually reaching a depth of about 500 m, but by this time the elevation has dropped off below the saturation horizon, so from this point on the carbonate sediments are overlaid by red clay.

If we drill a hole down through a part of the ocean floor that is presently below the saturation horizon, the top part of the drill core will consist of clay, followed by CaCO_3 at greater depths. The core may also contain regions in which silica predominates. Since silica production is very high in equatorial regions, the appearance of such a layer suggests that this particular region of the oceanic crust has moved across the equator.

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2.4: Chemical budgets of oceanic elements

To the extent that the composition of the ocean remains constant, the rate at which any one element is introduced into seawater must equal the rate of its removal. A listing of the various routes of addition and removal, together with the estimated rate of each process, constitutes the budget for a given element. If that budget is greatly out of balance and no other transport routes are apparent, then it is likely that the ocean is not in a steady state with respect to that element, at least on a short time scale. It is important to understand, however, that short-term deviations from constant composition are not necessarily inconsistent with a long-term steady state. Deviations from the latter condition are most commonly inferred from geological evidence.

The major input of elements to the oceans is river water. Groundwater seepage constitutes a very small secondary source. These were considered the only sources until the 1970's, when the existence of hydrothermal springs at sites of seafloor spreading became known. There are presently no reliable estimates of the magnitude of this source. Pollution represents an additional input, mainly dissolved in river water, but also sometimes in rain and by dry deposition.

Routes of removal are formation and burial of sediments, formation of evaporite deposits, direct input to the atmosphere by sea-salt aerosol transfer associated with bubble-breaking, and burial with sediments, either in interstitial water or adsorbed onto active surfaces. Reaction with newly-formed basalt associated with undersea volcanic activity appears to be an important removal mechanism for some elements.

Table 7: Input and output rates of major elements in seawater by two routes. The units are Tg y⁻¹. The other major routes involve interaction with the seafloor through hydrothermal vents and incorporation into sediments, but only river input and loss to the atmosphere are quantifiable with any degree of accuracy.

Species	Addition from Rivers	Loss to Atmosphere
Cl ⁻	308	40
Na ⁺	269	21
S (mostly SO ₄ ²⁻)	143	4
Mg ²⁺	137	3
K ⁺	52	1
Ca ²⁺	550	0.5
HCO ₃ ⁻	1980	
H ₄ SiO ₄	180	

Phosphorus

The major elements undergoing steady-state dynamic change in the ocean are connected with biological processes. The key limiting element in the development of oceanic biomass is phosphorus, in the form of the phosphate ion. For terrestrial plant life, nitrogen is more commonly the limiting element, where it is taken up in the form of the nitrate ion. In the ocean, however, the ratio of the nitrate ion concentration to that of phosphorus has been found to be everywhere the same; this implies that the concentration of one controls that of the other. The source of nitrate ion is atmospheric N₂, which is freely soluble in water and is thus always present in abundance. The conversion of N₂ to NO₃⁻ is presumed to be biologically mediated, probably by bacteria. The constancy of the NO₃⁻/P concentration ratio implies that the phosphorus concentration controls the activity of the nitrogen-fixing organisms, and thus the availability of nitrogen to oceanic life.

Photosynthetic activity in the upper part of the ocean causes inorganic phosphate to be incorporated into biomass, reducing the concentration of phosphorus; in warm surface waters, phosphate may become totally depleted. A given phosphorus atom may be traded several times among the plant, animal and bacterial populations before it eventually finds itself in biodebris (a dead organism or a fecal pellet) that falls into the deep part of the sea. Only about 1% of the phosphorus atoms that descend into deeper waters actually reach the bottom, where they are incorporated into sediments and permanently removed from circulation. The other 99% are released in the form of soluble phosphate, which is eventually brought to the surface in regions of upwelling. An average phosphorus atom will undergo one cycle of this circulation in about 1000 years; only a few months of this cycle will be spent in biomass. After an average of 100 such cycles, the atom will be removed from circulation and locked into the bottom sediment, and a new one will have entered the sea with river or juvenile water.

Phosphorus is unique in that its major source of input to the oceans derives ultimately from pollution; in the long term, this represents a transfer of land-based phosphate deposits to the oceans. About half of the phosphorus input is in the form of suspended material, both organic and inorganic, the latter being in a variety of forms including phosphates adsorbed onto clays and iron oxide particles, and calcium phosphate (apatite) eroded from rocks. These various particulates are known to dissolve to some extent once they reach the ocean, but there is considerable uncertainty about the rates of these processes under various conditions.

The major sink for oceanic phosphorus is burial with organic matter; this accounts for about two-thirds of the phosphorus removed. Most of the remainder is due to deposition with CaCO_3 . A minor removal route is through reaction with Fe(II) formed when seawater attacks hot basalt, and in the formation of evaporite deposits. However, there is more phosphorus in evaporite deposits in the Western U.S. than in all of the ocean, so it is apparent that the long-term phosphorus budget is still not clearly understood.

Carbon

Carbon enters the ocean from both the atmosphere (as CO_2) and river water, in which the principal species is HCO_3^- . Once in solution, the carbonate species are in equilibrium with each other and with H_3O^+ , and the concentrations of all of these are influenced by the partial pressure of atmospheric CO_2 . The mass budget for calcium is linked to that of carbon through solubility equilibria with the various solid forms of CaCO_3 (mainly calcite). During photosynthesis, C^{12} is taken up slightly more readily than the rare isotope C^{13} . Since the rate of photosynthesis is controlled by the phosphate concentration, the $\text{C}^{13}/\text{C}^{12}$ ratio in the dissolved carbon dioxide of surface waters is slightly higher than in the ocean as a whole. Observations of carbon isotope ratios in buried sediments have been useful in tracking historical changes in phosphate concentrations.

The C:P ratio and the regulation of atmospheric CO_2

The ratio of carbon to phosphorus in sea salt is about eight times greater than the same ratio measured in organic debris. This implies that in exhausting the available phosphate, the living organisms in the upper ocean consume only 12.5% of the dissolved carbon. Even this relatively small withdrawal of carbon from the carbonate system is sufficient to noticeably reduce the partial pressure of gaseous CO_2 in equilibrium with the ocean; it has been estimated that if all life in the ocean should suddenly cease, the atmospheric CO_2 content would rise to about three times its present level. The regulation of atmospheric CO_2 pressure by the oceans also works the other way: since the amount of dissolved carbonate in the oceans is so much greater than the amount of CO_2 in the atmosphere, the oceans act to buffer the effects of additions of CO_2 to the atmosphere. Calculations indicate that about half of the CO_2 that has been produced by burning fossil fuel since the Industrial Revolution has ended up in the oceans.

Bicarbonate

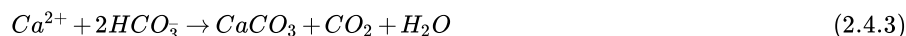
This is of course the major carbonate species in the ocean. Although it is interconvertible with CO_2 and is thus coupled to the carbon and photosynthetic cycles, itself can neither be taken up nor produced by organisms, and so it can be treated somewhat independently of biological activity. In this sense the only major input of into the oceans is river water. The two removal mechanisms are formation of CO_2



and the (biologically mediated) formation of CaCO_3 :



Since the pH of the oceans does not change, H^+ is conserved and the removal of HCO_3^- by biogenic secretion of CaCO_3 can be expressed by the sum of these reactions:



whose reverse direction represents the dissolution of the skeletal remains of dead organisms as they fall to lower depths.

Calcite

The upper parts of the ocean tend to be supersaturated in CaCO_3 . Solid CaCO_3 , in the form of calcite, is manufactured by a large variety of organisms such as foraminifera. A constant rain of calcite falls through the ocean as these organisms die. The solubility of increases with pressure, so only that portion of the calcite that falls to shallow regions of the ocean floor is incorporated into sediments and removed from circulation; the remainder dissolves after reaching a depth known as the lysocline. At the present time, the amounts of carbonate and Ca^{2+} supplied by erosion and volcanism appear to be only about one-third as great as the amount of calcite produced by organisms. As the carbonate concentration in a given region of the ocean becomes depleted due to higher calcite production, the lysocline moves up, tending to replenish the carbonate, and reducing the amount that is withdrawn by burial in sediments. Organic residues that fall into the deep sea are mostly oxidized to CO_2 , presumably by bacterial activity.

Other Elements

Calcium

Calcium is removed from seawater solely by biodeposition as CaCO_3 , a process whose rate can be determined quite accurately both at the present and in the past.

Table 2.4.1: Present-day budget for oceanic calcium (Tg Ca/yr).

--	--

inputs		outputs	
rivers	550	CaCO ₃ into shallow water	520
volcanic basalt	191	CaCO ₃ into deep water	440
cation exchange	37		
total	778		960

As is explained above, the upper part of the ocean is supersaturated in calcite but the lower ocean is not. For this reason, less than 20% of the CaCO₃ that is formed ends up as sediment and is eventually buried.

The main questions about the calcium budget tend to focus on the rates and locales at which dissolution of skeletal carbonates occurs, and on how to interpret the various kinds of existing carbonate sediments. For example, the crystalline form aragonite is less stable than calcite, and will presumably dissolve at a higher elevation. The absence of aragonite-containing pteropod shells in deeper deposits seems to confirm this, but in the absence of rate data is it difficult to know at what elevations these particular organisms originated.

The data in the above Table indicate that at the present time there is a net removal of calcium from the oceans. This is due to the rise in sea level since the decline of the more recent glacial epoch during the past 11,000 years. The additional water has covered the continental shelves, increasing the amount of shallow ocean where the growth of organisms is most intense. Over the more distant past (25 million years) the calcium budget appears to be well balanced.

Chloride

Evidence from geology and paleontology indicates that the salinity, and hence the chloride concentration of seawater has been quite constant for about 600 million years. There have been periods when climatic conditions and coastal topography have led to episodes of evaporite formation, but these have evidently been largely compensated by the eventual return of the evaporite deposits to the sea. The natural input of chloride from rivers is about 215 Tg/yr, but the present input is about half again as great (Table 7 on page 33), due to pollution. Also, there are presently no significant areas where seawater is evaporating to dryness. Thus the oceanic chloride budget is considerably out of balance. However, the replacement time of Cl⁻ in the oceans is so long (87 million years) that this will probably have no long-term effect.

Sodium

Although sodium is tied to chloride, it is also involved in the formation of silicate minerals, the weathering of rocks, and in cation exchange with clay sediments. Its short-term budget is quite out of balance for the same reasons as is that of chloride. On a longer time scale, removal of sodium by reaction with hot basalt associated with undersea volcanic activity may be of importance.

Sulfate

Considerably more sulfate is being added to seawater than is being removed by the major mechanisms of sediment formation (mainly CaSO₄ and pyrites). The natural river input is 82 Tg of S per year, while that due to pollution is 61 Tg/yr from rivers and 17 Tg/yr from rain and dry deposition.

Magnesium

This element is unusual in that its river-water input is balanced mostly by reaction with volcanic basalt; removal through biogenic formation of magnesian calcite (dolomite) accounts for only 11% of its total removal from the ocean. The present-day magnesium budget seems to have been balanced for the past 100 million years. However, most of the extensive dolomite deposits were formed prior to this time, so the longer-term magnesium budget is poorly understood.

Potassium

The potassium budget of the ocean is not well understood. The element is unusual in that only about 60% of its input is by rivers; the remainder is believed to come from newly formed undersea basalt. The big question about potassium is how it is removed; fixation by ion-exchange with illite clays seems to be a major mechanism, and its uptake by basalt (at lower temperatures than are required for its release) is also believed to occur.

Silica

About 85% of the silicon input to the oceans comes from river water in the form of silicic acid, H₄SiO₄. The remainder probably comes from basalt. It is removed by biogenic deposition as opaline silica, SiO₂·n H₂O produced mainly by planktonic organisms (radiolaria and diatoms). Unlike the case for CaCO₃, the ocean is everywhere undersaturated in silica, especially near the surface where these organisms deplete it with greater efficiency than any other element.

Because opaline silica dissolves so rapidly, only a small fraction makes it to the bottom. The major deposits occur in shallower waters where coastal upwelling provides a good supply of N and P nutrients for siliceous organisms. Thus over half of the biogenic silica deposits are found in the Antarctic ocean.

In spite of the fact that dissolved silica has the shortest replacement time (21,000 years) of any major element in the ocean, its concentration appears to have been remarkably constant during geological time. This is taken as an indication of the ability of siliceous organisms to respond quickly to changes in local concentrations of dissolved silica.

Nitrogen

This element is complicated by its biologically-mediated exchange with atmospheric nitrogen, and by its existence in several oxidation states, all of which are interconvertible. Unlike the other major elements, nitrogen does not form extensive sedimentary deposits; most of the nitrogen present in dead organic material seems to be removed before it can be buried. Through this mechanism there is extensive cycling of nitrogen between the shallow and deep parts of the oceans.

The real difficulty in constructing a budget for oceanic nitrogen is the very large uncertainty in the rates of the major input (fixation) and output. Both of these processes are biologically mediated, but little is known about what organisms are responsible, where they thrive and how they are affected by local nutrient supply and other conditions.

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CHAPTER OVERVIEW

3: The Atmosphere

Life as we know it on the Earth is entirely dependent on the tenuous layer of gas that clings to the surface of the globe, adding about 1% to its diameter and an insignificant amount to its total mass. And yet the atmosphere serves as the earth's window and protective shield, as a medium for the transport of heat and water, and as source and sink for exchange of carbon, oxygen, and nitrogen with the biosphere. The atmosphere acts as a compressible fluid tied to the earth by gravitation; as a receptor of solar energy and a thermal reservoir, it constitutes the working fluid of a heat engine that transports and redistributes matter and energy over the entire globe. The atmosphere is also a major temporary repository of a number of chemical elements that move in a cyclic manner between the hydrosphere, atmosphere, and the upper lithosphere. Finally, the atmosphere is a site for a large variety of complex photochemically initiated reactions involving both natural and anthropogenic substances.

[3.1: Structure and Composition of the Atmosphere](#)

[3.2: Origin and Evolution of the Atmosphere](#)

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3.1: Structure and Composition of the Atmosphere

Life as we know it on the Earth is entirely dependent on the tenuous layer of gas that clings to the surface of the globe, adding about 1% to its diameter and an insignificant amount to its total mass. And yet the atmosphere serves as the earth's window and protective shield, as a medium for the transport of heat and water, and as source and sink for exchange of carbon, oxygen, and nitrogen with the biosphere. The atmosphere acts as a compressible fluid tied to the earth by gravitation; as a receptor of solar energy and a thermal reservoir, it constitutes the working fluid of a heat engine that transports and redistributes matter and energy over the entire globe. The atmosphere is also a major temporary repository of a number of chemical elements that move in a cyclic manner between the hydrosphere, atmosphere, and the upper lithosphere. Finally, the atmosphere is a site for a large variety of complex photochemically initiated reactions involving both natural and anthropogenic substances.

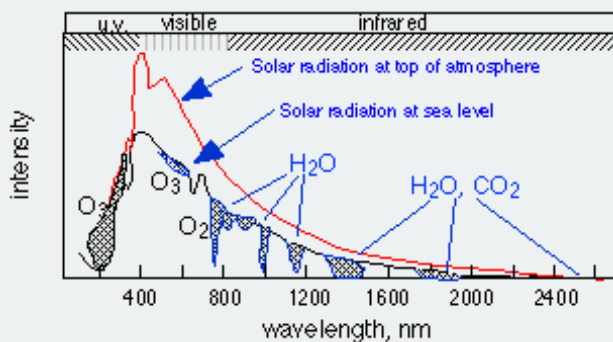
On the scale of cubic meters the air is a homogeneous mixture of its constituent gases, but on a larger scale the atmosphere is anything but uniform. Variations of temperature, pressure, and moisture content in the layers of air near the earth's surface give rise to the dynamic effects we know as the weather.

Although the density of the atmosphere decreases without limit with increasing height, for most practical purposes one can roughly place its upper boundary at about 500 km. However, half the mass of the atmosphere lies within 5 km, and 99.99% within 80 km of the surface. The average atmospheric pressure at sea level is 1.01×10^5 pascals, or 1010 millibars. A 1-cm^2 cross section of the earth's surface supports a column weighing 1030 g; the total mass of the atmosphere is about 5.27×10^{21} g.

About 80% of the mass of the atmosphere resides in the first 10 km; this well-mixed region of fairly uniform composition is known as the *troposphere*.

Solar irradiation of the Earth

The gases ozone, water vapor, and carbon dioxide are only minor components of the atmosphere, but they exert a huge effect on the Earth by absorbing radiation in the ranges indicated by the shading. Ozone in the upper atmosphere filters out the ultraviolet light below about 360 nm that is destructive of life. O_2 , H_2O , CO_2 and CH_4 are "greenhouse" gases that trap some of the heat absorbed from the Sun and prevent it from re-radiating back into space.

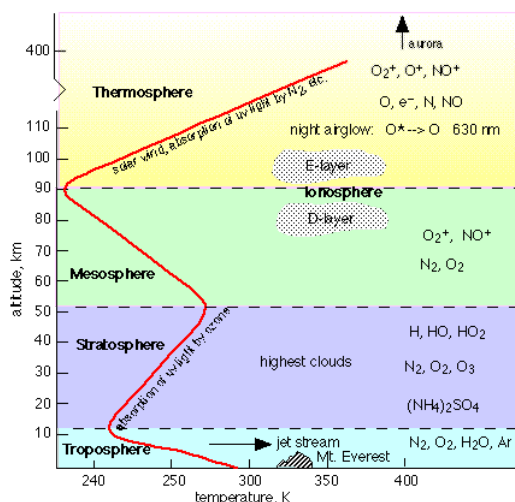


Structure of the atmosphere

We commonly think of gas molecules as moving about in a completely random manner, but the Earth's gravitational field causes downward motions to be very slightly favored so that the molecules in any thin layer of the air collide more frequently with those in the layer below. This gives rise to a pressure gradient that is the most predictable and well known structural characteristic of the atmosphere. This gradient is described by an exponential law which predicts that the atmospheric pressure should decrease by 50% for every 6 km increase in altitude. This law also predicts that the composition of a gas mixture will change with altitude, the lower-molecular weight components being increasingly favored at higher altitudes. However, this gravitational fractionation effect is completely obliterated below about 160 km owing to turbulence and convective flows (winds).

The atmosphere is divided vertically into several major regions which are distinguished by the sign of the temperature gradient. In the lowermost region, the troposphere, the temperature falls with increasing altitude. The major source of heat input into this part of the atmosphere is long-wave radiation from the earth's surface, while the major loss is radiation into space.

At higher elevations the temperature begins to rise with altitude as we move into a region in which heat is produced by exothermic chemical reactions, mainly the decomposition of ozone that is formed photochemically from dioxygen in the stratosphere. At still higher elevations the ozone gives out and the temperature begins to drop; this is the mesosphere, which is finally replaced by the thermosphere which consists largely of a plasma (gaseous ions). This outer section of the atmosphere which extends indefinitely to perhaps 2000 km is heated by absorption of intense u.v. radiation from the Sun and also from the solar wind, a continual rain of electrons, protons, and other particles emitted from the Sun's surface.



Structure of the atmosphere. The main divisions of the atmosphere are defined by the elevations at which the sign of the temperature gradient changes. The chemical formulas at the right show the major species of interest in the various regions. The shaded D- and E-layers are regions of high ion concentrations that reflect radio waves and are important in long-distance communication.

Composition of the atmosphere

Except for water vapor, whose atmospheric abundance varies from practically zero up to 4%, the fractions of the major atmospheric components N_2 , O_2 , and Ar are remarkably uniform below about 100 km. At greater heights, diffusion becomes the principal transport process, and the lighter gases become relatively more abundant. In addition, photochemical processes result in the formation of new species whose high reactivities would preclude their existence in significant concentrations at the higher pressures found at lower elevations.

The atmospheric gases fall into three abundance categories: major, minor, and trace. Nitrogen, the most abundant component, has accumulated over time as a result of its geochemical inertness; a very small fraction of it passes into the other phases as a result of biological activity and natural fixation by lightning. It is believed that denitrifying bacteria in marine sediments may provide the major route for the return of N_2 to the atmosphere. Oxygen is almost entirely of biological origin, and cycles through the hydrosphere, the biosphere, and sedimentary rocks. Argon consists mainly of Ar^{40} which is a decay product of K^{40} in the mantle and crust.

Table 1: Major components

nitrogen	N_2	78.08 %
oxygen	O_2	20.95 %
argon	Ar	0.93 %

The most abundant of the minor gases aside from water vapor is carbon dioxide, about which more will be said below. Next in abundance are neon and helium. Helium is a decay product of radioactive elements in the earth, but neon and the other inert gases are primordial, and have probably been present in their present relative abundances since the earth's formation. Two of the minor gases, ozone and carbon monoxide, have abundances that vary with time and location. A variable abundance implies an imbalance between the rates of formation and removal. In the case of carbon monoxide, whose major source is anthropogenic (a small amount

is produced by biological action), the variance is probably due largely to localized differences in fuel consumption, particularly in internal combustion engines. The nature of the carbon monoxide sink (removal mechanism) is not entirely clear; it may be partly microbial.

Table 2: Minor components

water	H ₂ O	0-4 %
carbon dioxide	CO ₂	325 ppm
neon	Ne	18 ppm
helium	He	5 ppm
methane	CH ₄	2 ppm
krypton	Kr	1 ppm
hydrogen	H ₂	0.5 ppm
nitrous oxide	N ₂ O	0.3 ppm
carbon monoxide	CO	0.05-0.2 ppm
ozone	O ₃	0.02 - 10 ppm
xenon	Xe	0.08 ppm


Table 3: Trace components

ammonia	NH ₃	4 ppb
nitrogen oxide	NO	1 ppb
sulfur dioxide	SO ₂	1 ppb
hydrogen sulfide	H ₂ S	0.05 ppb

Ozone

Ozone is formed by the reaction of O₂ with oxygen atoms produced photochemically. As a consequence the abundance of ozone varies with the time of day, the concentration of O atoms from other sources (photochemical smog, for example), and particularly with altitude; at 30 km, the ozone concentration reaches a maximum of 12 ppm.

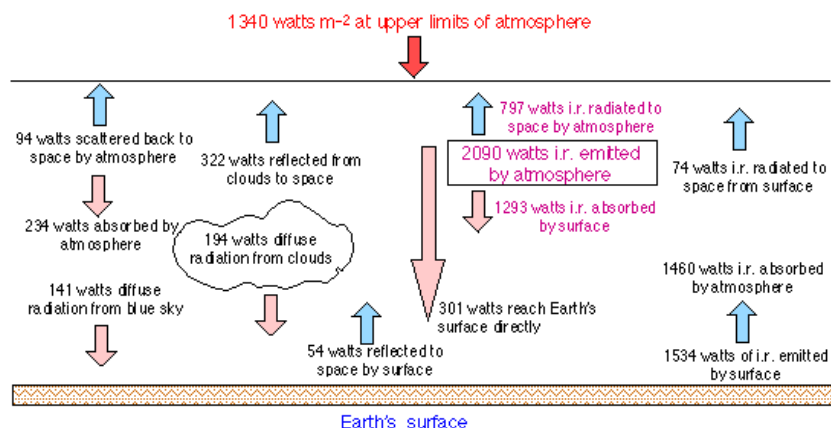
Carbon dioxide

The concentration of atmospheric carbon dioxide, while fairly uniform globally, is increasing at a rate of 0.2-0.7% per year as a result of fossil fuel burning. The present CO₂ content of the atmosphere is about 129  10¹⁸ g. Most of the CO₂, however, is of natural origin, and represents the smallest part of the total carbonate reservoir that includes oceanic CO₂, HCO₃⁻, and carbonate sediments. The latter contain about 600 times as much CO₂ as the atmosphere, and the oceans contain about 50 times as much. These relative amounts are controlled by the rates of the reactions that interconvert the various forms of carbonate.

The surface conditions on the earth are sensitively dependent on the atmospheric CO₂ concentration. This is due mainly to the strong infrared absorption of CO₂, which promotes the absorption and trapping of solar heat (see below). Since CO₂ acts as an acid in aqueous solution, the pH of the oceans is also dependent on the concentration of CO₂ in the atmosphere; it has been estimated that if only 1% of the carbonate presently in sediments were still in the atmosphere, the pH of the oceans would be 5.9, instead of the present 8.2.

Energy balance of the atmosphere and earth

The amount of energy (the solar flux) impinging on the outer part of the atmosphere is $1367 \text{ watts m}^{-2}$. About 30% of this is reflected or scattered back into space by clouds, dust, and the atmospheric gas molecules themselves, and by the earth's surface. About 19% of the radiation is absorbed by clouds or the atmosphere (mainly by O_3 , but not CO_2), leaving 51% of the incident energy available for absorption by the earth's surface. If one takes into account the uneven illumination of the earth's surface and the small flux of internal heat to the surface, the assumption of thermal equilibrium requires that the earth emit about 240 watts m^{-2} . This corresponds to the power that would be emitted by a black body at 255 K, or -18°C , which is the average temperature of the atmosphere at an altitude of 5 km. The observed mean global surface temperature of the earth is 13°C , and is presumably the temperature required to maintain thermal equilibrium between the earth and the atmosphere.



The greenhouse effect

The energy radiated by the earth has a longer wavelength (maximum 12m) than the incident radiation. Most gases absorb radiation in this range quite efficiently, including those gases such as CO_2 and N_2O that do not absorb the incident radiation. The energy absorbed by atmospheric gases is re-radiated in all directions; some of it therefore escapes into space, but a portion returns to the earth and is reabsorbed, thus raising its temperature. This is commonly called the greenhouse effect. If the amount of an infrared-absorbing gas such as carbon dioxide increases, a larger fraction of the incident solar radiation is trapped, and the mean temperature of the earth will increase.

Any significant increase in the temperature of the oceans would increase the atmospheric concentrations of both water and CO_2 , producing the possibility of a runaway process that would be catastrophic from a human perspective. Fossil fuel combustion and deforestation during the last two hundred years have increased the atmospheric CO_2 concentration by 25%, and this increase is continuing. The same combustion processes responsible for the increasing atmospheric CO_2 concentration also introduce considerable quantities of particulate materials into the upper atmosphere. The effect of these would be to scatter more of the incoming solar radiation, reducing the amount that reaches and heats the earth's surface. The extent to which this process counteracts the greenhouse effect is still a matter of controversy; all that is known for sure is that the average temperature of the Earth is increasing.

Nitrous oxide

Carbon dioxide is not the only atmospheric gas of anthropogenic origin that can affect the heat balance of the earth; other examples are SO_2 and N_2O . Nitrous oxide is of particular interest, since its abundance is fairly high, and is increasing at a rate of about 0.5% per year. It is produced mainly by bacteria, and much of the increase is probably connected with introduction of increased nitrate into the environment through agricultural fertilization and sewage disposal. Besides being a strong infrared absorber, N_2O is photochemically active, and can react with ozone. Any significant depletion of the ozone content of the upper atmosphere would permit more ultraviolet radiation to reach the earth. This would have numerous deleterious effects on present life forms, as well as contributing to a temperature increase. The warming effect attributed to anthropogenic additions of greenhouse gases to the atmosphere is estimated to be about 2 watts per m^2 , or about 1.5% of the $150 \text{ watts per m}^2$ trapped by clouds and atmospheric gases. This is a relatively large perturbation compared to the maximum variation in solar output of $0.5 \text{ watts per m}^2$ that has been observed during the past century. Continuation of greenhouse gas emission at present levels for another century could increase the atmospheric warming effect by 6-8 watts per m^2 .

A less-appreciated side effect of the increase in atmospheric carbon dioxide (and of other plant nutrients such as nitrates) may be reduction in plant species diversity by selectively encouraging the growth of species which are ordinarily held in check by other species that are able to grow well with fewer nutrients. This effect, for which there is already some evidence, could be especially pronounced when the competing species utilize the C_3 and C_4 photosynthetic pathways that differ in their sensitivity to CO_2 .

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3.2: Origin and Evolution of the Atmosphere

Prebiotic atmosphere

The atmosphere of the Earth (and also of Venus and Mars) is generally believed to have its origin in relatively volatile compounds that were incorporated into the solids from which these planets accreted. Such compounds could include nitrides (a source of N₂), water (which can be taken up by silica, for example), carbides, and hydrogen compounds of nitrogen and carbon. Many of these compounds (and also some noble gases) can form clathrate complexes with water and some minerals which are fairly stable at low temperatures. The high temperatures developed during the later stages of accretion as well as subsequent heating produced by decay of radioactive elements presumably released these gases to the surface. Even at the present time, large amounts of CO₂, water vapor, N₂, HCl, SO₂ and H₂S are emitted from volcanoes. The more reactive of these gases would be selectively removed from the atmosphere by reaction with surface rocks or dissolution in the ocean, leaving an atmosphere enriched in its present major components with the exception of oxygen which is discussed in the next section.

Any hydrogen present would tend to escape into space, causing the atmosphere to gradually become less reducing. However there is now some doubt that hydrogen and other volatiles (mainly the inert gases) were present in the newly accreted planets in anything like their cosmic abundance. The main evidence against this is the observation that gases such as helium, neon and argon, which are among the ten most abundant elements in the universe, are depleted on the earth by factors of 10⁻⁷ to 10⁻¹¹. This implies that there was a selective removal of these volatiles prior to or during the planetary accretion process.

The overall oxidation state of the earth's mantle is not consistent with what one would expect from equilibration with highly reduced volatiles, and there is no evidence to suggest that the composition of the mantle has not remained the same. If this is correct, then the primitive atmosphere may well have had about the same composition as the gases emitted by volcanoes at the present time. These consist mainly of water and CO₂, together with small amounts of N₂, H₂, H₂S, SO₂, CO, CH₄, NH₃, HCl and HF. If water vapor was a major component of outgassing of the accreted earth, it must have condensed quite rapidly into rain. Any significant concentration of water vapor in the atmosphere would have led to a runaway greenhouse effect, resulting in temperatures as high as 400°C.

Origin of Atmospheric Oxygen

Free oxygen is never more than a trace component of most planetary atmospheres. Thermodynamically, oxygen is much happier when combined with other elements as oxides; the pressure of O₂ in equilibrium with basaltic magmas is only about 10⁻⁷ atm. Photochemical decomposition of gaseous oxides in the upper atmosphere is the major source of O₂ on most planets. On Venus, for example, CO₂ is broken down into CO and O₂. On the earth, the major inorganic source of O₂ is the photolysis of water vapor; most of the resulting hydrogen escapes into space, allowing the O₂ concentration to build up. An estimated 2 × 10¹¹ g of O₂ per year is generated in this way. Integrated over the earth's history, this amounts to less than 3% of the present oxygen abundance. The partial pressure of O₂ in the prebiotic atmosphere is estimated to be no more than 10⁻³ atm, and may have been several orders of magnitude less. The major source of atmospheric oxygen on the earth is photosynthesis carried out by green plants and certain bacteria:



A historical view of the buildup of atmospheric oxygen concentration since the beginning of the sedimentary record (3.7 × 10⁹ ybp) can be worked out by making use of the fact that the carbon in the product of the above reaction has a slightly lower C¹³ content than does carbon of inorganic origin. Isotopic analysis of carbon-containing sediments thus provides a measure of the amounts of photosynthetic O₂ produced at various times in the past.

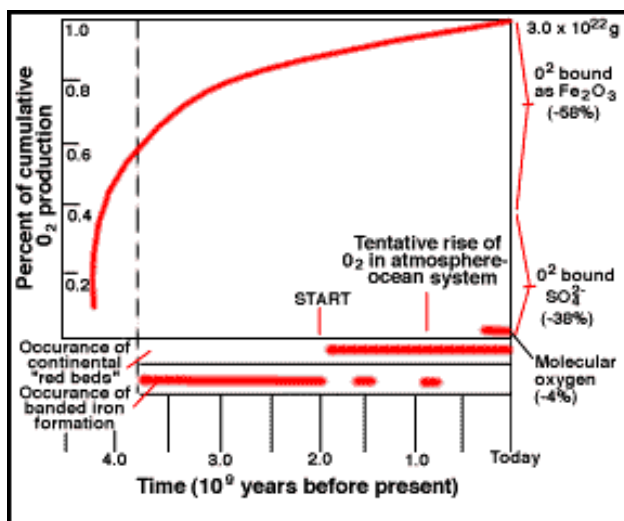
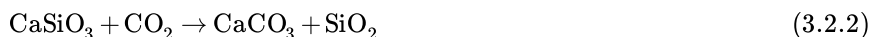


Figure 3.2.1: Evolution of atmospheric oxygen content. Note carefully that the curve plots cumulative O_2 production, but that until a few hundred million years ago, most of this was taken up by $Fe(II)$ compounds in the crust and by reduced sulfur; only after this massive "oxygen sink" became filled did free O_2 begin to accumulate in the atmosphere.

Carbon Dioxide

Carbon dioxide has probably always been present in the atmosphere in the relatively small absolute amounts now observed (around $54 \times 10^{15} \text{ mol} = 54 \text{ Pmol}$). The reaction of CO_2 with silicate-containing rocks to form precambrian limestones suggest a possible moderating influence on its atmospheric concentration throughout geological time.



About ten percent of the atmospheric CO_2 is taken up each year by [photosynthesis](#). Of this, all except 0.05 percent is returned by *respiration*, almost entirely due to microorganisms. The remainder leaks into the slow part of the geochemical cycle, mostly as buried carbonate sediments.

Since the advent of the industrial revolution in 1860, the amount of CO_2 in the atmosphere has been increasing. Isotopic analysis shows that most of this has been due to fossil-fuel combustion; in recent years, the mass of carbon released to the atmosphere by this means has been more than ten times the estimated rate of natural removal into sediments. The large-scale destruction of tropical forests, which has accelerated greatly in recent years, is believed to exacerbate this effect by removing a temporary sink for CO_2 .

The oceans have a large absorptive capacity for CO_2 owing to its reaction with carbonate:



There is about 60 times as much inorganic carbon in the oceans as in the atmosphere. However, efficient transfer takes place only into the topmost (100 m) wind-mixed layer of the ocean, which contains only about one atmosphere equivalent of CO_2 . Further uptake is limited by the very slow transport of water into the deep ocean, which takes around 1000 years. For this reason, the buffering effect of the oceans on atmospheric CO_2 is not very effective; only about ten percent of the added CO_2 is taken up by the oceans.

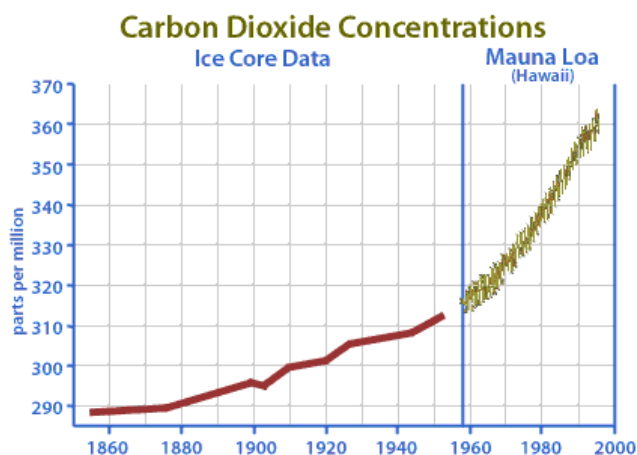


Figure. This set of plots, taken from an [ETE page](#) with data from NASA, shows the dramatic increase in atmospheric CO₂ since the beginning of the industrial age. The "squiggles" on the Mauna Loa data reflect seasonal variations; more CO₂ is taken up during the longer-daylight periods of the summer.

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CHAPTER OVERVIEW

4: The Biosphere

The biosphere comprises the various regions near the earth's surface that contain and are dynamically affected by the metabolic activity of the approximately 1.5 million animal species and 0.5 million plant species that are presently known and are still being discovered at a rate of about 10,000 per year. The biosphere is the youngest of the dynamical systems of the earth, having had its genesis about 2 billion years ago. It is also the one that has most profoundly affected the other major environmental systems, particularly the atmosphere and the hydrosphere.

[4.1: Chemistry and Energetics of the Life Process](#)

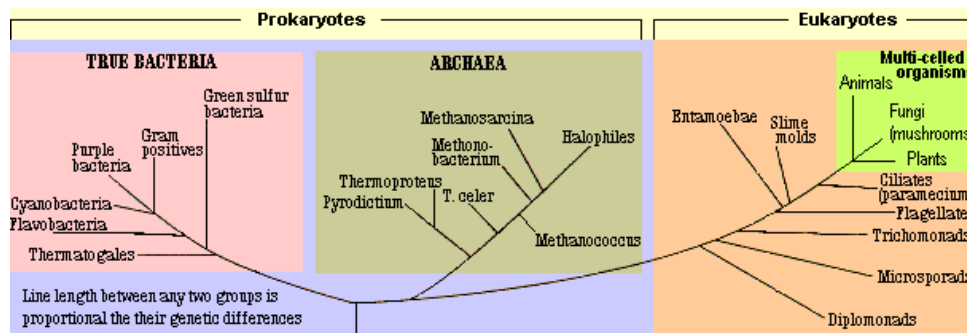
[4.2: Biogeochemical Evolution](#)

[4.3: Gaia - Bioregulation of the Environment](#)

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4.1: Chemistry and Energetics of the Life Process

The biosphere comprises the various regions near the earth's surface that contain and are dynamically affected by the metabolic activity of the approximately 1.5 million animal species and 0.5 million plant species that are presently known and are still being discovered at a rate of about 10,000 per year. The biosphere is the youngest of the dynamical systems of the earth, having had its genesis about 2 billion years ago. It is also the one that has most profoundly affected the other major environmental systems, particularly the atmosphere and the hydrosphere.



"The tree of life"

About a third of the chemical elements cycle through living organisms, which are responsible for massive deposits of silicon, iron, manganese, sulfur, and carbon. Large quantities of methane and nitrous oxide are introduced into the atmosphere by bacterial action, and plants alone inject about 400,000 tons of volatile substances (including some metals) into the atmosphere annually.

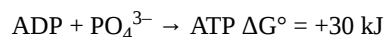
It has been suggested that biological activity might be responsible for the deficiency of hydrogen on Earth, compared to its very high relative abundance in the solar system as a whole. Bacteria capable of reducing hydrogen compounds into H_2 transform this element into a form in which it can escape from the earth; such bacteria may have been especially active in the reducing atmosphere of the early planet.

A second mechanism might be the microbial production of methane, which presently injects about 10^9 T of CH_4 into the atmosphere each year. Some of this reaches the stratosphere, where it is oxidized to CO_2 and H_2O . The water vapor is photolyzed to H_2 , which escapes into space. This may be the major mechanism by which water vapor (and thus hydrogen) is transported to the upper atmosphere; the low temperature of the upper atmosphere causes most of the water originating at lower levels to condense before it can migrate to the top of the atmosphere.

The increase in the abundance of atmospheric oxygen from its initial value of essentially zero has without question been the most important single effect of life on earth, and the time scale of this increase parallels the development of life forms from their most primitive stages up to the appearance of the first land animals about 0.5 billion years ago.

Bioenergetics

All life processes involve the uptake and storage of energy, and its subsequent orderly release in small steps during the metabolic process. This energy is taken up in the combination of ADP with inorganic phosphate to form ATP, in which form the energy is stored and eventually delivered to sites where it can provide the free energy needed for driving non-spontaneous reactions such as protein and carbohydrate synthesis.



The three main metabolic processes are glycolysis, respiration, and photosynthesis. The first two of these extract free energy from glucose by breaking it up into smaller, more thermodynamically stable fragments. Photosynthesis reverses this process by capturing the energy of sunlight into ATP which then drives the buildup of glucose from CO_2 .

Glycolysis and fermentation.

As its name implies, this most primitive (and least efficient) of all metabolic processes is based on the breakdown of a sugar into fragments having a smaller total free energy. Thus the 6-carbon sugar glucose can be broken down into two 3-carbon lactic acid units, or into three 2-carbon ethanol units.

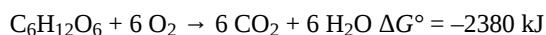


In this process, two molecules of ATP are produced, thus capturing 61 kJ of free energy. Since the standard free energy of glucose (with respect to its elements) is -2870 kJ , this represents an overall efficiency of about 2 percent.

The net reaction of glycolysis is essentially a rearrangement of the atoms initially present in the energy source. This is a form of fermentation, which is defined as the enzymatic breakdown of organic molecules in which other organic compounds serve as electron acceptors. Since there is no need for an external oxidizing or reducing agent, there is no change in the oxidation state of the environment.

Respiration

When the enzymatic degradation of organic molecules is accompanied by transfer of electrons to an external (and usually better) electron acceptor, the process is known as respiration. The overall reaction of respiration is the oxidation of glucose to carbon dioxide:



In this process, 36 molecules of ADP are converted into ATP, thus capturing 1100 kJ of free energy: an efficiency of 38 percent.

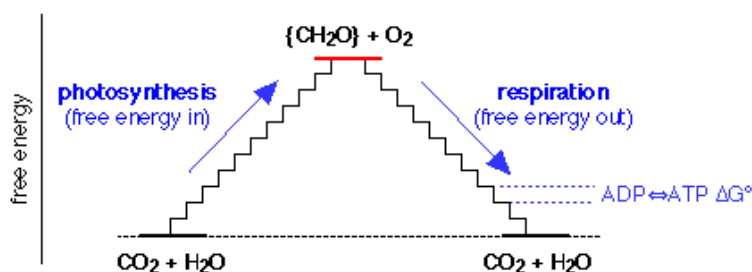
The oxidizing agent (electron sink) need not be oxygen; some bacteria reduce nitrates to NO or to N_2 , and sulfates or sulfur to H_2S . These metabolic products can have far-reaching localized environmental effects, particularly if hydrogen ions are involved. Falling down the respiratory ladder presents a succinct picture of oxidation-reduction and the role of non- O_2 electron sinks in biological energy capture.

Photosynthesis

The energy of sunlight is trapped in the form of an intermediate which is able to deliver electrons to successively lower free-energy levels through the mediation of various molecules (mainly cytochromes) comprising an electron-transport chain. The free energy thus gained is utilized in part to reduce CO_2 to glucose, which is then available to supply metabolic energy by glycolysis or respiration. In green plants and eukaryotic algae, the source of hydrogen is water, the net reaction being



For every CO_2 molecule fixed in this way, 469 kJ of free energy must be supplied. Red light of 680 nm wavelength has an energy of 168 kJ/mol; this implies that about three photons must be absorbed for every carbon atom taken up, but experiment indicates that about ten seem to be required.



The photosynthetic - respiration cycle.

Photosynthesis utilizes the energy of red light to add hydrogen (from H_2O) and electrons (from the O in H_2O) to CO_2 , reducing it to **carbohydrate**. **Respiration** is the reverse of this process; electrons are removed from the carbohydrate (food is "burned") in small steps, each one releasing a small amount of energy. Some of this energy is liberated as heat, but part of it is used to add a phosphate group to ADP, converting it into ATP. **ATP** (adenosine triphosphate) is to an organism's energy needs as money is to our material needs; it circulates to wherever it is required in order to bring about energy-requiring reactions or to make muscle cells contract. Each increment of energy given up by ATP converts it back to ADP and phosphate, ready to repeat the cycle.

Green plants are able to operate in both modes during the daylight hours, reverting to respiration-only at night. **Animals** carry out only the right side of the cycle and thus require as source of carbohydrate ("**food**") either directly (by eating plants), or indirectly by eating other animals that eat plants.

There are many kinds of photosynthetic bacteria, but with one exception (cyanobacteria) they are incapable of using water as a source of hydrogen for reducing carbon dioxide. Instead, they consume hydrogen sulfide or other reduced sulfur compounds,

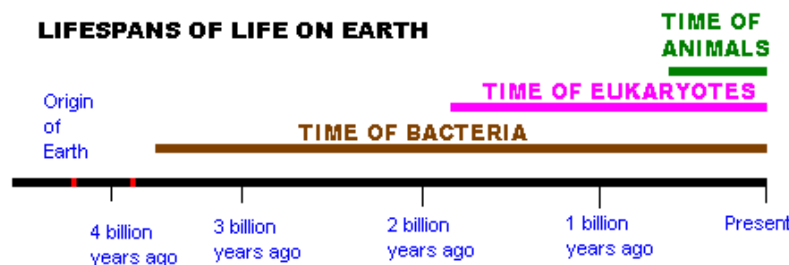
organic molecules, or elemental hydrogen itself, excreting the reducing agent in an oxidized state. Green plants, cyanobacteria, green filamentous bacteria and the purple nonsulfur bacteria utilize glucose by respiration during periods of darkness, while the green sulfur bacteria and the purple sulfur bacteria are strictly anaerobic.

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4.2: Biogeochemical Evolution

Present evidence suggests that blue-green algae, and possibly other primitive microbial forms of life, were flourishing 3 billion years ago. This brackets the origin of life to within one billion years; prior to 4 billion years ago, surface temperatures were probably above the melting point of iron, and there was no atmosphere nor hydrosphere.

By about 3.8 billion years ago, or one billion years after the earth was formed, cooling had occurred to the point where rain was possible, and primitive warm, shallow oceans had formed. The atmosphere was anoxic and highly reducing, containing mainly CO_2 , N_2 , CO , H_2O , H_2S , traces of H_2 , NH_3 , CH_4 , and less than 1% of the present amount of O_2 , probably originating from the photolysis of water vapor. This oxygen would have been taken up quite rapidly by the many abundant oxidizable substances such as Fe(II) , H_2S , and the like.



Timeline for development of the major life forms.

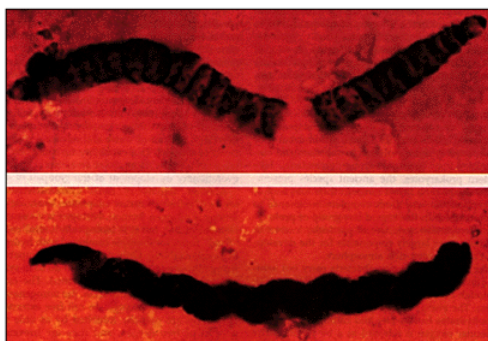
Evidence for early life

The fossil record that preserves the structural elements of organisms in sedimentary deposits has for some time provided a reasonably clear picture of the evolution of life during the past 750,000 years. In more recent years, this record has been considerably extended, as improved techniques have made it possible to study the impressions made by single-celled microorganisms embedded in rock formations.

The main difficulty in studying fossil microorganisms extending back beyond a billion years is in establishing that the relatively simple structural forms one observes are truly biogenic. There are three major kinds of evidence for this.

- Many of the most **primitive life forms are still thriving**, and these provide useful models with which some of the fossil forms can be compared.
- **Carbon isotope ratios** provide a second independent line of evidence for early life, or at least that of photosynthetic origin. In photosynthesis, C^{12}O_2 is taken up slightly more readily than is the heavier (and rarer) isotope C^{13}O_2 ; thus all but the very earliest life forms have left an isotopic fossil record even though the structural fossil may no longer be identifiable.
- A third evidence for early life is any indication of the **presence of free oxygen** in the local environment. Easily oxidizable species such as Fe(II) were very widely distributed on the primitive earth, and could not remain in contact with oxygen for very long without being oxidized. The oldest known formations of oxidized iron pyrite and of uranite are in sediments that were laid down between 2.0 and 2.3 billion years ago.

If all three of these lines of evidence are present in samples that can be shown to be contemporaneous with the sediments in which they are found, then the argument for life is incontrovertible. One of the most famous of these sites was discovered near Thunder Bay, Ontario in the early 1950's. The Gunflint Formation consists of an exposed layer of chert (largely silica) from which the overlying shale of the Canadian Shield had been removed. Microscopic examination of thin sections of this rock revealed a variety of microbial cell forms, including some resembling present freshwater blue-green algae. Also present in the Gunflint Deposits are the oldest known examples of metazoa, or organisms which display a clear differentiation into two or more types of cell. These deposits have been dated at 1.9-2.0 billion years.



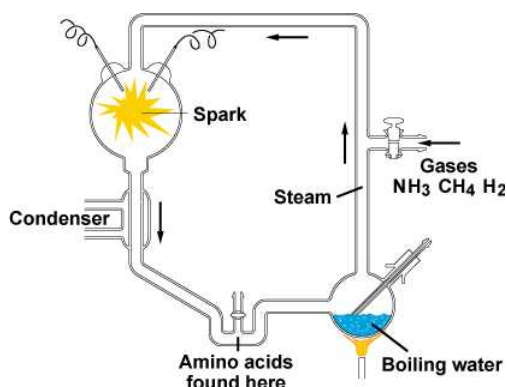
These filaments are believed to be the fossilized imprints of blue-green algae, one of the earliest life forms. They occur in the Bitter Springs Formation in Australia and are about 850 million years old.

The evidence from very old paleomicrobiotic deposits is less clear. Western Australia has yielded fossil forms that are apparently 2.8 billion years old, and other deposits in the same region contain structures resembling living blue-green algae. Other forms, heavily modified by chemical infiltration, bear some resemblance to a present iron bacterium, and are found in sediments laid down 3.5 billion years ago, but evidence that these fossils are contemporaneous with the sediments in which they are found is not convincing.

The oldest evidence of early life is the observed depletion of C^{13} in 3.8-billion year old rocks found in southwestern Greenland.

Origin of life: the organic environment

Under the conditions that prevailed at this time, most organic molecules would be thermodynamically stable, and there is every indication that a rich variety of complex molecules would be present. The most direct evidence of this comes from laboratory experiments that attempt to simulate the conditions of the primitive environment of this period, the first and most famous of these being the one carried out by Stanley Miller in 1953.



Schematic of the Miller experiment. A mixture of the various reduced gases believed to be compose the early atmosphere circulate through an apparatus in which spark discharges (intended to simulate lightning) create a complex mixture of organic compounds.

S.L. Miller: A production of amino acids under possible primitive earth conditions. 1953: Science (117) 528-529. U. Texas provided the above diagram, and contains a very good description of of primitive life with many pictures of fossil organisms.

Since that time, other experiments of a similar nature have demonstrated the production of a wide variety of compounds under prebiotic conditions, including nearly all of the monomeric components of the macromolecules present in living organisms. In addition, small macromolecules, including peptides and sugars, as well as structural entities such as lipid-based micelles, have been prepared in this way.

The discovery in 1989 of a number of amino acids in the iridium-rich clay layer at the Cretaceous-Tertiary boundary suggests that bio-precursor molecules can be formed or deposited during a meteoric impact. Although this particular event occurred only 65 million years ago (and is presumed to be responsible for the extinction of the dinosaurs), the Earth has always been subject to meteoric impacts, and it is conceivable that these have played a role in the origin of life.

The presence of clays, whose surfaces are both asymmetric and chemically active, could have favored the formation of species of a particular chirality; a number of experiments have shown that clay surfaces can selectively adsorb amino acids which then form small peptides. It has been suggested that the highly active and ordered surfaces of clays not only played a crucial role in the formation of life, but might have actually served as parts of the first primitive self-replicating life forms, which only later evolved into organic species.

The first organisms

Since no laboratory experiment has yet succeeded in producing a self-replicating species that can be considered living, the mechanism by which this came about in nature must remain speculative. Infectious viruses have been made in the laboratory by simply mixing a variety of nucleotide precursors with a template nucleic acid and a replicase enzyme; the key to the creation of life is how to do the same thing without the template and the enzyme.

Smaller polynucleotides may have formed adventitiously, possibly on the active surface of an inorganic solid. These could form complementary base-paired polymers, which might then serve as the templates for larger molecules. Non-enzymatic template-directed synthesis of nucleotides has been demonstrated in the laboratory, but the resulting polymers have linkages that are not present in natural nucleotides.

It has been suggested that these linkages could have been selectively hydrolyzed by a long period of cycling between warm, cool, wet, and dry environmental conditions. The earth at that time was rotating more rapidly than it is now; cycles of hydration-dehydration and of heating-cooling would have been more frequent and more extreme.

The first organisms would of necessity have been heterotrophs— that is, they derived their metabolic energy from organic compounds in the environment. Their capacity to synthesize molecules was probably very limited, and they would have had to absorb many key substances from their surroundings in order to maintain their metabolic activity. Among the most primitive organisms of this kind are the archaeons, which are believed to be predecessors of both bacteria and eucaryotes. DNA sequencing of one such organism, a methane-producer that lives in ocean-bottom sediments at 200 atm and 48-94°C, reveals that only about a third of the genes resemble those of bacteria or eucaryotes.

It has been estimated that about 50 genes are required in order to define the minimal biochemical and structural machinery that a hypothetical simplest possible cell would have.

Development of photosynthetic organisms

The earliest organisms derived their metabolic energy from the organic substances present in their environment; once they began to reproduce, this nutrient source began to become depleted.

Some species had probably by this time developed the ability to reduce carbon dioxide to methane; the hydrogen source could at first have been H_2 itself (at that time much more abundant in the atmosphere), and later, various organic metabolites from other species could have served.

Before the food supply neared exhaustion, some of these organisms must have developed at least a rudimentary means of absorbing sunlight and using this energy to synthesize metabolites. The source of hydrogen for the reduction of CO_2 was at first small organic molecules; later photosynthetic organisms were able to break this dependence on organic nutrients and obtain the hydrogen from H_2S .

These bacterial forms were likely the dominant form of life for several hundred million years. Eventually, due perhaps to the failing supply of H_2S , plants capable of mediating the photochemical extraction of hydrogen from water developed. This represented a large step in biochemical complexity; it takes 10 times as much energy to abstract hydrogen from water than from hydrogen sulfide, but the supply is virtually limitless.

It appears that photosynthesis evolved in a kind of organism whose present-day descendants are known as cyanobacteria.

Procaryotes and eucaryotes

The five “kingdoms” into which living organisms are classified are Monera, Protista (protozoans, algae), Fungi, Plantae, and Animalia. The genetic (and thus, evolutionary) relations between these and the subcategories within them are depicted below.

Superimposed on this, however, is an even more fundamental division between the procaryotes and eucaryotes.

Prokaryotes

In this group are primitive organisms whose single cells contain no nucleus; the gene-bearing structure is a single long DNA chain that is folded irregularly throughout the cell. Prokaryotic cells usually reproduce by budding or division; where sexual reproduction does occur, there is a net transfer of some genetic material from one cell to another, but there is never an equal contribution from both parents.

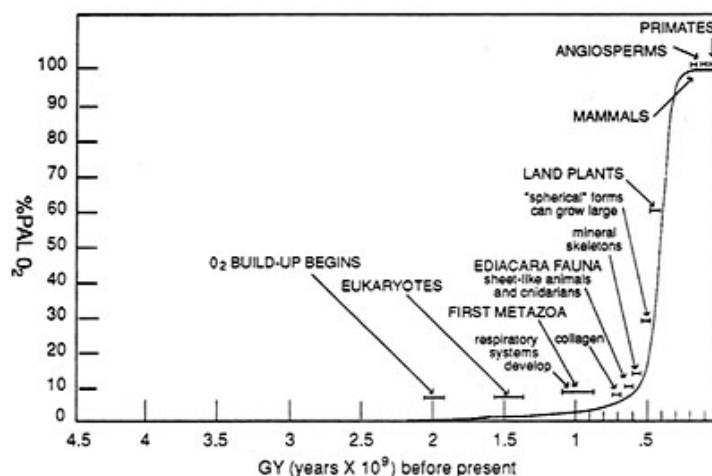
In spite of their primitive nature, prokaryotes constitute the majority of organisms in the biosphere. The division between bacteria and archaea within the prokaryotic group is a fairly recent one. Archaea are now believed to be the most primitive of all organisms, and include the so-called extremophiles that occupy environmental niches in which life was at one time thought to be impossible; they have been found in sedimentary rocks, hot springs, and highly saline environments.

Eukaryotes.

All other organisms— seaweeds (algae), protozoa, molds, fungi, animals and plants, are composed of eukaryotic cells. These all have a membrane-bound nucleus, and with a few exceptions they all reproduce by mitosis, in which the chromosomes split longitudinally and move toward opposite poles. Other organelles unique to eukaryotes are mitochondria, ribosomes, and structural elements such as microtubules.

Oxygen and biogeochemical evolution

Oxygen is poisonous to all forms of life in the absence of enzymes that can reduce the highly reactive byproducts of oxidation and oxidative metabolism (peroxides, superoxides, etc.). All organic compounds are thermodynamically unstable in the presence of oxygen; carbon-carbon double bonds in lipids are subject to rapid attack. Prebiotic chemical evolution leading to the development of biopolymers was possible only under the reducing, anoxic conditions of the primitive atmosphere.



The rise of atmospheric oxygen. Once organisms existed that could use water as a hydrogen source for the reduction of carbon dioxide, O_2 began to be introduced into the atmosphere. The widespread occurrence of ferrous compounds in surface rocks and sediments provided a sink for this oxygen that probably did not become saturated until about 2 billion years ago, when the atmospheric oxygen abundance first rose above about 1 percent. Illustration from *All about entropy, the laws of thermodynamics, and order from disorder*. There is lots of good stuff here!

As the oxygen concentration began to rise, organisms in contact with the atmosphere had to develop protective mechanisms in order to survive. One indication of such adaptation is the discovery of fossil microbes whose cell walls are unusually thick. A more useful kind of adaptation was the synthesis of compounds that would detoxify oxygen by reacting rapidly either with O_2 itself or with peroxides and other active species derived from it. Isoprenoids (the precursors of steroids) and porphyrins are examples of two general classes of compounds that are found in nearly all organisms, and which may have originated in this way. Later, highly efficient oxygen mediating enzymes such as peroxidase and catalase developed. The widespread phenomenon of bioluminescence may be the result of a very early adaptation to oxygen. The compound luciferin is a highly efficient oxygen detoxifier, which also happens to be able to emit light under certain conditions. Bioluminescence probably developed as a by-product in early prokaryotic organisms, but was gradually lost as more efficient detoxifying mechanisms became available.

Development of the eucaryotes

In spite of the deleterious effects of oxygen on cell biomolecules, O_2 is nevertheless an excellent electron sink, capable of releasing large quantities of energy through the oxidation of glucose. This energy can be efficiently captured through oxidative phosphorylation, the key process in respiration.

A cell that utilizes oxygen must have a structural organization that isolates the oxygen-consuming respiratory centers from the other parts of the cell that would be poisoned by oxygen or its reaction products. Some procaryotic organisms have developed in this way; a number of cyanobacteria and other species are facultative anaerobes which can survive both in the presence and absence of oxygen.

It is in the eucaryotic cell, however, that this organization is fully elaborated; here, respiration occurs in membrane-bound organelles called mitochondria. With only a few exceptions, all eucaryotic organisms are obligate aerobes; they can rarely survive and can never reproduce in the absence of oxygen. Mitotic cell division depends on the contractile properties of the protein actomyosin, which only forms when oxygen is present.

The development of the eucaryotic cell about 1.4 billion years ago is regarded as the most significant event in the evolution of the earth and of the biosphere since the appearance of photosynthesis and the origin of life itself. How did it come about? The present belief, supported by an increasing amount of evidence, suggests that it began when one species of organism engulfed another. The ingested organism possessed biochemical machinery not present in the host, but which was retained in such a way that it conferred a selective evolutionary advantage on the host. Eventually the two organisms became able to reproduce as one, and so effectively became a single organism. This process is known as *endosymbiosis*.

According to this view, mitochondria represent the remains of a primitive oxygen-tolerant organism that was incorporated into one that could produce the glucose fuel for the oxygen to burn. Chloroplasts were once free-living photosynthesizing procaryotes similar to present-day cyanobacteria. It is assumed that some of these began parasitising respiratory organisms, conferring upon them the ability to synthesize their carbohydrate food during daylight. The immense selective advantage of this arrangement is evident in the extent of the plant kingdom.

Consequences of the oxygen increase

It is interesting that an atmospheric oxygen concentration of about 1 percent, known as the *Pasteur point* is both the maximum that obligate anaerobes can tolerate, and the minimum required for oxidative phosphorylation.

Louis Pasteur discovered that some bacteria are anaerobic and unable to tolerate oxygen above 1% concentration.

As was mentioned previously, the oxygen produced by the first photosynthetic organisms was taken up by ferrous iron in sediments and surface minerals. The widespread deposits known as banded iron formations consist of alternating layers of Fe(III)-containing oxides (hematite and magnetite) that were laid down between 1 and 2 billion years ago; the layering may reflect changing climatic or other environmental conditions that brought about a cycling of the organism population.

During the buildup of oxygen, an equivalent amount of carbon had to be deposited in sediments in order to avoid the thermodynamically spontaneous back reaction which would consume the O_2 through oxidation of the organic matter. Thus the present levels of atmospheric oxygen are due to a time lag in the geochemical cycling of photosynthetic products.

As the oxygen concentration increased, evolution seems to have speeded up; this may reflect both the increased metabolic efficiency and the greater biochemical complexity of the eucaryotic cell. The oldest metazoan (multiple-celled) fossils are coelenterates that appeared about 700 million years ago. Modern representatives of this group such as marine worms and jellyfish can tolerate oxygen concentrations as low as 7%, thus placing a lower boundary on the atmospheric oxygen content of that era. The oldest fossil organisms believed to have possessed gills, which function only above 10% oxygen concentration, appeared somewhat later. Carbon dioxide decreased as oxygen increased, as indicated by the prevalence of dolomite over limestone in early marine sediments.

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4.3: Gaia - Bioregulation of the Environment

The Gaia Hypothesis

The physical conditions under which life as we know it can exist encompass a relatively narrow range of temperature, pH, osmotic pressure, and ultraviolet radiation intensity. It seems remarkable enough that life was able to get started at all; it is even more remarkable that it has continued to thrive in the face of all the perils that have, or could have occurred, during the past 3 billion years or so.

During the time that life has been evolving, the sun has also been going through the process of evolution characteristic of a typical star; one consequence of this is an increase in its energy output by about 30 percent during this time. If the sun's output should suddenly drop to what it was 3 billion years ago, the oceans would freeze. How is it that the earth was not in a frozen state for the first 1.5 billion years of life's existence? Alternatively, if conditions were somehow suitable 3 billion years ago, why have the oceans not long since boiled away?

A rather non-traditional answer to this kind of question is that the biosphere is far from playing a passive role in which it is continually at the mercy of environmental conditions. Instead, the earth's atmosphere, and to a lesser extent the hydrosphere, may be actively maintained and regulated by the biosphere. This view has been championed by the British geochemist J.E. Lovelock, and is known as the *Gaia hypothesis*.

Gaia is another name for the Greek earth-goddess Ge, from which root the sciences of geography, geometry, and geology derive their names. Lovelock's book Gaia: a new look at life on Earth (Oxford, 1979) is a short and highly readable discussion of the hypothesis.

Evidence in support of this hypothesis is entirely circumstantial, but nevertheless points to important questions that must be answered: how have the climatic and chemical conditions on the earth remained optimal for life during all this time; how can the chemical composition of the atmosphere remain in a state that is tens of orders of magnitude from equilibrium?

Note

Although the Gaia hypothesis has received considerable publicity in the popular press, it has never been very well received by the scientific community, many of whom feel that there is no justification for proposing a special hypothesis to describe a set of connections which can be quite adequately explained by conventional geochemical processes. More recently, even Lovelock has backed away from the teleological interpretation of these relations, so that the Gaia hypothesis should now be more properly described as a set of loosely connected effects, rather than as a hypothesis. Nevertheless, these effects and the mechanisms that might act to connect them are sufficiently interesting that it seems worthwhile to provide an overview of the major observations that led to the development of the hypothesis.

Teleology is the doctrine that natural processes operate with a purpose. See *No longer willful, Gaia becomes respectable*. 1988: Science 240 393-395.

Bioregulation of the Atmosphere

The increase in the oxygen content of the atmosphere as a result of the development of the eucaryotic cell was discussed above. Why has the oxygen content leveled off at 21 percent? It is interesting to note that if the oxygen concentration in the atmosphere were only four percent higher, even damp vegetation, once ignited by lightning, would continue to burn, enveloping vast areas of the earth in a firestorm. Evidence for such a worldwide firestorm that may be related to the extinction of the dinosaurs has recently been discovered. The charcoal layers found in widely distributed sediments laid down about 65 million years ago are coincident with the iridium anomaly believed to be due to the collision of a large meteor with the earth.

- **Oxygen:** Regulation of the oxygen partial pressure is probably achieved by a balance between its production through photosynthesis and its consumption during oxidation of organic matter; the present steady state requires the burial of about 0.1% the carbon that is fixed annually, leaving one O₂ molecule in the air for each atom of carbon removed from the photosynthetic cycle. The large quantities of microbially-produced methane and N₂O also constitute important oxygen sinks; if methanogenic bacteria should suddenly cease to exist, the O₂ concentration would rise by 1% in about 12,000 years. This type of regulation implies a negative feedback mechanism, in which an increase in atmospheric oxygen would increase the activity of organisms capable of generating metabolic products that react with it.

- **Nitrous oxide:** Nitrous oxide, in addition to serving as an oxygen sink, might also be a factor in the regulation of the intensity of the ultraviolet component of sunlight. N_2O acts as a catalytic intermediate in the decomposition of stratospheric ozone, which shields the earth from excessive ultraviolet radiation.
- **Ammonia:** Ammonia, another atmospheric gas, is produced by the biosphere in approximately the same quantities as methane, 10^9 tons per year, and at the expense of a considerable amount of metabolic energy. The function of NH_3 could well be to regulate the pH of the environment; in the absence of ammonia, the large amounts of SO_2 and HCl produced by volcanic action would reduce the pH of rain to about 3. The fact that the atmospheric concentration of ammonia is only 10^{-8} times that of N_2 should not imply that this “trace” component plays a less significant role in the overall nitrogen cycle than does N_2 . In fact, the annual rates of production of the two gases are roughly the same; the much lower steady-state concentration of NH_3 is due to its faster turnover time.
- **Nitrogen:** As stable as the triply-bonded N_2 molecule is, there is a still more stable form of nitrogen: the hydrated nitrate ion. How is this stability consistent with the predominance of nitrogen in the atmosphere? The answer is that it is not: if it were not for nitrogen-fixing bacteria (powered directly or indirectly by the free energy of ATP captured from sunlight), the nitrogen content of the atmosphere would disappear to almost zero. This would raise the oxygen fraction to disastrously high levels, and the additional NO_3^- concentration would increase the ionic strength and osmotic pressure of seawater to levels inconsistent with most forms of life.

Bioregulation of the Oceans

The input of salts into the sea from streams and rivers is about 5.4×10^8 tons per year, into a total volume of about $1.2 \times 10^9 \text{ km}^3$ yr^{-1} . Upwelling of juvenile water and hydrothermal action at oceanic ridges provide additional inputs of salts. With a few bizarre exceptions such as the brine shrimp and halophilic bacteria, 6 percent is about the maximum salinity level that organisms can tolerate. The internal salinities of cells must be maintained at much lower levels (around 1%) to prevent denaturation of proteins and other macromolecules whose conformations are dependent on electrostatic forces. At higher levels than this, the electrostatic interaction between the salt ions and the cell membrane destroys the integrity of the latter so that it can no longer pump out salt ions that leak in along the osmotic gradient. At the present rate of salt input, the oceans would have reached their present levels of salinity millions of years ago, and would by now have an ionic strength far too high to support life, as is presently the case in the landlocked Dead Sea.

The present average salinity of seawater is 3.4 percent. The salinity of blood, and of many other intra- and intercellular fluids in animals, is about 0.8 percent. If we assume that the first organisms were approximately in osmotic equilibrium with seawater, then our body fluids might represent “fossilized” seawater as it existed at the time our predecessors moved out of the sea and onto the land.

By what processes is salt removed from the oceans in order to maintain a steady-state salinity? This remains one of the major open questions of chemical oceanography. There are a number of answers, mostly based on strictly inorganic processes, but none is adequately supported by available evidence. For example, Na^+ and Mg^{2+} ions could adsorb to particulate debris as it drops to the seafloor, and become incorporated into sediments. The requirement for charge conservation might be met by the involvement of negatively charged silicate and hydroxyaluminum ions. Another possible mechanism might be the burial of salt beds formed by evaporation in shallow, isolated arms of the sea, such as the Persian Gulf. Extensive underground salt deposits are certainly found on most continents, but it is difficult to see how this very slow mechanism could have led to an unfluctuating salinity over shorter periods of highly variable climatic conditions.

The possibility of biological control of oceanic salinity starts with the observation that about half of the earth's biomass resides in the sea, and that a significant fraction of this consists of diatoms and other organisms that build skeletons of silica. When these organisms die, they sink to the bottom of the sea and add about 300 million tons of silica to sedimentary rocks annually. It is for this reason that the upper levels of the sea are undersaturated in silica, and that the ratio of silica to salt in dead salt lakes is much higher than in the ocean.

These facts could constitute a basis for a biological control of the silica content of seawater; any link between silica and salt could lead to the control of the latter substance as well. For example, the salt ions might adsorb onto the silica skeletons, and be carried down with them; if the growth of these silica-containing organisms is itself dependent on salinity, we would have our negative feedback mechanism.

The continual buildup of biogenic sedimentary deposits on the ocean floor might possibly deform the thin oceanic crust by its weight, and cause local heating by its insulating properties. This could conceivably lead to volcanic action and the formation of new land mass, thus linking the lithosphere into Gaia.

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