

EVOLUTION OF EARTH'S ATMOSPHERE

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The Diversity of Planetary Atmosphere

Although the planets Mercury, Venus, Earth, and Mars have masses within a single order of magnitude range, they possess atmospheres with extremely different properties (Table 1). These bodies may have initially possessed primordial atmospheres of solar composition whose dominant light gases (hydrogen and helium) were lost to space and replaced by outgassed water, carbon dioxide, and nitrogen (and small amounts of other gases) during the final phase of accretion 4.5 billion years (Ga) ago. The divergence in atmospheric composition seen today may in part reflect differences in initial volatile abundance, but much of the diversity can be attributed to the individual evolutionary paths of these atmospheres over the age of the Solar System. Rates of planetary atmospheric evolution have differed markedly: whereas the other planets have suffered catastrophic atmospheric evolution (Mercury has experienced complete loss, Venus a runaway greenhouse and devolatilization of surface rocks, and Mars has lost most of the atmosphere to space or the crust), the evolution of Earth's atmosphere has been comparatively mild. Both external processes, such as radiation and the corpuscular wind from the Sun and impacts, and internal processes, such as volcanism and recycling of a planet's crust (e.g., plate tectonics) control this evolution. While some processes drive exchange of compounds between the atmosphere and reservoirs in the surface, oceans, or interiors of planets, or the interconversion of different chemical species, others result in the secular, irreversible evolution of the atmosphere. Examples of

Table 1 The atmospheres of the inner planets Mercury, Venus, Earth, and Mars

Planet	Mass [Earths]	Pressure (hPa)	Composition
Mercury	0.053	10^{-9}	H, He, Na
Venus	0.817	90 000	96% CO ₂ , 3% N ₂ , minor CO, SO ₂
Earth	1	1 000	78% N ₂ , 21% O ₂ , 1% Ar, minor H ₂ O, CO ₂
Mars	0.107	7	95% CO ₂ , 3% N ₂ , 2% Ar, minor CO, O ₂

the former include atmospheric photochemistry, volcanism, and plate tectonics. The latter include the accretion of new material (impacts of comets or meteorites), escape of hydrogen to space, and the sequestration of certain elements (siderophiles) into the metallic core.

Earth's atmosphere has been profoundly affected by another process: life. The modern atmosphere, containing abundant oxygen in gross chemical disequilibrium with surface organic carbon and gases such as methane, is testament to life's ability to efficiently convert light energy into chemical energy, some of which is stored in the chemical disequilibrium between the atmosphere and surface. Significant disequilibrium is not present on the sterile worlds of Venus and Mars, and it has been suggested that the simultaneous presence of pairs of gases like O₂ and CH₄ in an atmosphere may serve as a planetary 'biosignature' that reveals the presence of abundant life even at a distance. Some gases such as CO₂, the principal source of biological reduced carbon, are maintained at mixing ratios much lower than the level predicted in the absence of life. The current terrestrial atmosphere is far from the end state reached by Venus, where all of the surface volatiles are in the atmosphere (Table 2).

Also in contrast to neighboring planets, the terrestrial atmosphere maintains conditions suitable for life (providing a modest greenhouse effect and a shield against biologically harmful radiation), and has apparently done so for 3.5 billion years, despite a 40% increase in solar luminosity, giant impacts, and the

Table 2 The reservoirs of the major volatiles on the Earth (mantle quantities are uncertain)

	Reservoir	Size (hPa)	Climate role
H ₂ O	Atmosphere	<0.001	Greenhouse gas, carbonate sink, weathering, biology, plate tectonics
	Ocean	26	
	Hydrated crust	10	
	Mantle	~100	
	Total	136	
CO ₂	Atmosphere	0.00003	Greenhouse gas
	Ocean	0.0002	
	Carbonate rocks	4	
	Mantle	~26	
	Total	30	
N ₂	Atmosphere	0.078	Buffer gas, enhances effect of greenhouse gases
	Crustal rocks	0.025	
	Mantle	~0.1	
	Total	0.2	

changing tempo of plate tectonics. This fact is even more remarkable in light of the relatively short residence time of most gases: water vapor, the most powerful greenhouse gas in the atmosphere, has a residence time of only 10 days before exchanging with the oceans. Even relatively inert nitrogen gas, the principal component of the atmosphere, is recycled by biological fixation (reduction), oxidation, and rereduction to N₂ on a time scale of 10–15 million years. Thus Earth's atmosphere is not only out of chemical equilibrium, but is dynamically maintained, having no intrinsic buffering capacity on geologic time scales.

Evolutionary Processes

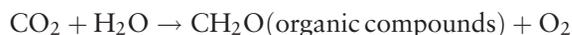
The early atmosphere would have been subject to frequent bombardment by planetesimals left over from early planetary accretion. These impacts may have brought in volatiles, but they may also have removed (to space) some of the existing atmosphere either by the momentum of the impact shock wave or heating of the upper atmosphere (see below). Impacts also turn over the crust and expose fresh surfaces, accelerating chemical interactions between the atmosphere and crustal rocks. Giant impact basins on the Moon date to 3.9 billion years in age, indicating that a similar bombardment shaped the Earth's atmosphere for the first several hundred million years of its history. A second process that may have profoundly (perhaps catastrophically) affected Earth's atmosphere was the formation of the iron–nickel core. This removal of metallic iron (and possible fractions of iron-soluble elements like sulfur, carbon, and hydrogen) left the Earth's surface and mantle in a considerably more oxidized chemical state, a condition that would have been reflected in the oxidation state of the compounds that were being outgassed by volcanoes. Thus, as is the case today, CO₂, N₂, and SO₂ were the dominant components of volcanic gases, rather than CH₄, H₂S, and NH₃.

Thermal escape of light atoms such as hydrogen and helium can occur from the exosphere (the uppermost layer of the atmosphere where the mean free path between collisions exceeds the scale height). Escape is efficient if the mean thermal speed is a significant fraction of the escape velocity such that a non-negligible number of molecules in the 'tail' of the Maxwellian (thermal) distribution have speeds above the escape velocity. Extreme and vacuum ultraviolet radiation from the Sun (mostly in the 121.4 nm Lyman α line of hydrogen) is absorbed and converted into heat in the Earth's thermosphere. The modern thermosphere lies above 400 km and has a temperature of 1200 K. Non-thermal escape mechanisms, driven by

photochemistry and other energetic processes, also operate. All these processes create energetic particles by photolytic, electron impact, or ionic reactions. In the absence of a magnetic field, direct momentum transfer may result in knocking atoms from the exosphere, in a process known as 'sputtering'. Ions may also migrate to the polar regions, where the magnetic field lines are open to the tail of the magnetosphere, and they can readily escape along these field lines. In charge exchange, H atoms lose an electron to a heavier ion, typically O⁺, and the resulting proton is accelerated by the electric field of the solar wind to exceed the escape velocity. The ionization potentials of O and H differ by only 0.02 eV. This difference is smaller than the thermal energies corresponding to typical upper-atmosphere temperatures, and as a consequence the charge transfer process is very efficient.

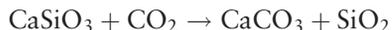
Hydrogen loss from the exosphere is very efficient, but the actual rate (3.0×10^8 atoms cm⁻² s⁻¹) of escape from the modern oxygen-containing atmosphere is limited by the transport of hydrogen from deeper in the atmosphere. Hunten's limiting flux theorem relates the maximum escape flux of hydrogen to the abundance of total hydrogen in the mesosphere, determined largely by the chemical sources and transport. The escape rates of hydrogen in the past were probably much higher than the present rate. The primary reason is that the early atmosphere probably lacked oxygen: on the modern Earth, hydrogen is 'trapped' by recombination with oxygen to form water in the lower atmosphere before it can reach the upper atmosphere and escape. A second reason is that the Sun was more active in the past, providing a higher flux of EUV radiation to power hydrogen escape. The flow of hydrogen may have been sufficiently massive as to cause the hydrodynamic escape of heavier gases by momentum transfer.

Biology contributes to atmospheric evolution by modulating the interconversion of compounds and the exchange of compounds between the atmosphere and other reservoirs. The paramount example of this is oxygenic photosynthesis, which in effect partitions CO₂ into organic carbon and oxygen:

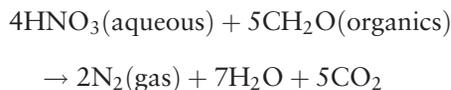


If the organic carbon is prevented from being immediately reoxidized (e.g., by combustion or by aerobic respiration in other organisms) then the oxygen can enter the atmosphere. At some point in the past photosynthetic production was able to overwhelm sinks of oxygen and the atmospheric mixing ratio of O₂ increased dramatically, an event that would never have occurred without the intervention of

biology. Biology is also responsible for repartitioning carbon dioxide between the atmosphere, oceans, and limestone rocks (kinetically favoring the last) by accelerating the process of silicate weathering and carbonate precipitation:



Without marine organisms, carbon dioxide levels would be much higher than current values: it has been suggested that the successive development of more sophisticated marine and terrestrial organisms (e.g., plants with vascular roots) has led to a secular decrease in atmospheric CO_2 over time. A third process where life has played an important role is to recycle oxides of nitrogen (specifically nitrates) back to the atmosphere by denitrification, e.g.:



In the absence of biology, the formation of nitrates by UV and lightning, and their rain out from the atmosphere, would have been unchecked, removing most N_2 (and thus most of the atmosphere!) in about one billion years.

Aerosols are a minor component of the terrestrial atmosphere whose importance to climate is only now being more fully understood. Aerosols are micrometer-sized particles of sulfur, organic compounds, and salts that remain suspended in the atmosphere for years. They scatter sunlight, effectively cooling the surface, and serve as cloud condensation nuclei, i.e., sites of cloud water droplet formation. Clouds can either cool (by reflecting sunlight back to space) or warm (by blocking the escape of infrared radiation). The aerosol content of the atmosphere may have evolved because of changes in ocean salinity, the surface area of the continents, and biological production of sulfur compounds and organic compounds.

The Record of Atmospheric Evolution

Because most of the atmosphere is recycled on a geologically short time scale, it has no 'memory' of anything but the most recent events in Earth history. The exceptions to this rule are the noble gases Ne, Ar, Kr, and Xe, elements that are chemically inert and too heavy to escape easily from the Earth. The rare gases in the terrestrial atmosphere are depleted with respect to other elements compared with their expected values in the primordial nebula that formed the planets. They also exhibit strong elemental and isotopic fractionation, such that heavier elements and isotopes are more abundant (Figure 1). The most plausible expla-

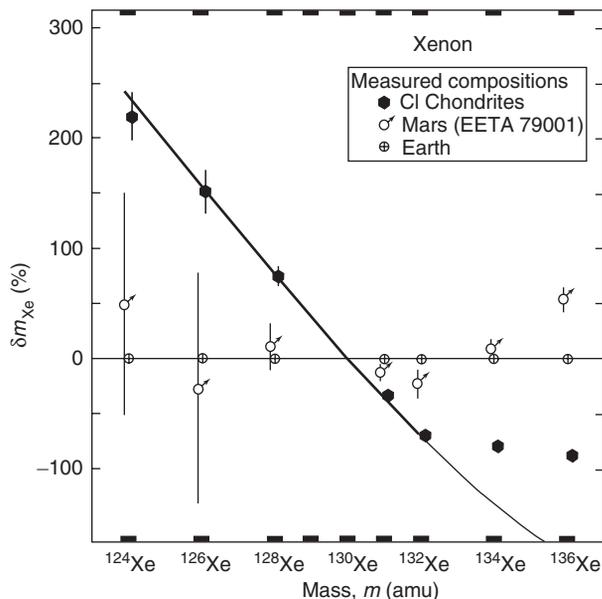


Figure 1 Evidence for loss of an early terrestrial atmosphere: isotopic composition of xenon in meteorites and in planetary atmospheres, plotted relative to terrestrial atmospheric xenon. Units are parts per thousand deviation from the terrestrial composition. The atmospheres of Earth and Mars are depleted in the light isotopes relative to meteorites, which are thought to reflect the composition of the primordial nebula. The lighter isotopes may have been carried away during the early escape of a hydrogen atmosphere. (After Pepin RO (1989) Atmospheric composition: key similarities and differences. In Atreya SK, Pollack JB, and Matthews MS (eds) *Origin and Evolution of Planetary and Satellite Atmospheres*. Tucson, AZ: University of Arizona Press. Reprinted with permission.)

nation is that these gases were components of a primordial atmosphere that escaped to space early in Earth history, perhaps in a hydrogen 'wind' driven by intense ultraviolet radiation from the young Sun or by the giant Moon-forming impact. (Terrestrial ^{40}Ar , in contrast to its sister isotopes ^{36}Ar and ^{38}Ar , is primarily a product of the radioactive decay of ^{40}K and therefore an exception.) Models of this escape also predict the loss of essentially all N- and C-containing compounds from such an atmosphere and imply that modern N and C have a separate, later origin, from a long-term reservoir in the Earth's interior or else from a late 'veener' of extraterrestrial material.

Our knowledge of the evolution of the other, reactive gases is obtained by examination of the chemical and physical effects the paleoatmosphere has had on materials preserved in the rock record. The best record, and the one that has received the most attention, is that for atmospheric oxygen. Much of this work is based on the disparate aqueous solubility of compounds of certain elements, particularly Fe, Mn, and U, in the presence or absence of atmospheric

oxygen. Under anoxic conditions, iron is in its highly soluble ferrous state, but insoluble ferric oxides and hydroxides form in the presence of even small amounts of oxygen. Sedimentary units formed in the Archean (3.8–2.5 Ga) and early Proterozoic (2.5–0.54 Ga) are characterized by banded iron formations, finely laminated deposits of iron oxides and carbonates. The distribution of these deposits suggests that iron was relatively mobile and hence oxygen was absent in the deep ocean during these epochs. Whether oxygen was present in shallower water is not clear: Iron is conspicuously rare in carbonate formations such as stromatolites from this time. Conversely, iron concentration in Archean paleosols (ancient soils) is low, indicating that Fe remained mobile (and hence removable) during the weathering process. If these soils were in chemical equilibrium with the atmosphere then the stability of the ferrous state constrained p_{O_2} levels to $<10^{-4}$ of the present atmospheric level (PAL). Oxidized soils and deposits (redbeds) in which the (ferric) iron is retained do not appear in the geologic record until after 2.4 Ga.

Reduced forms of mineral sulfur (pyrite) and uranium (uraninite) are insoluble and hence resistant to removal by aqueous process. These minerals are seen in Archean deposits, but not in later Proterozoic ones, again indicating an increase in atmospheric p_{O_2} . The ratio of thorium to uranium in mantle-derived rocks shows a marked increase from samples older than 2 Ga to younger samples, which can be explained if recycling of U into the mantle has become less efficient owing to increased retention of (soluble) U in an oxidizing hydrosphere. Manganese is oxidized only in the presence of abundant molecular oxygen, and on the modern Earth this occurs only through the intervention of Mn-oxidizing bacteria. Mn deposits appear only during certain intervals in the geologic record. The earliest Proterozoic was a unique period of Mn deposit formation (some of the deposits are of great economic importance). If these deposits were formed as oxides (rather than carbonates) then they would be unambiguous indicators of the appearance of high oxygen levels.

Although sulfur species are not a significant component of the present-day atmosphere, and the bulk of surface S is in the ocean, sulfur deposits may serve as indicators of past oxygen levels because the rate of oxidative weathering of sulfur minerals and the transfer of S as sulfate to the oceans is controlled by atmospheric O_2 . The other input of sulfur to the ocean–atmosphere system is SO_2 in volcanic gases. Variations in atmospheric oxygen will change the relative importance of these two sources. Possible evidence for such a change is the disappearance of iron formations after 1.8 Ga. Rather than being the result

of an oxidation event, the immobility of Fe could be the indirect result of a rise in atmospheric oxygen and the initiation of a ‘modern’ sulfur cycle, in which oxidative weathering of sulfur-bearing minerals on the continents leads to transport of sulfate to the oceans. Sulfate reduction (by bacteria) would produce elevated concentrations of sulfide in deep water and precipitation of Fe as pyrite. Sulfur from ancient marine sediments and evaporite deposits also records a shift in the distribution of relative abundance of the two major isotopes ^{32}S and ^{34}S , suggesting an increase in sulfate reduction by bacteria. In Archean rocks there is also evidence for mass-independent fractionation among a three-sulfur isotope system that includes ^{33}S (Figure 2). This fractionation pattern is unlike those produced by the oxidation of sulfur by weathering or the reduction of sulfate by biology, where fractionation is proportional to the mass differences between the isotopes. Mass-independent fractionation could indicate that in the absence of atmospheric oxygen during the Archean, certain gas-phase reactions were significant contributors to the sulfur cycle.

Carbon dioxide is a minor component (preindustrial $p_{\text{CO}_2} = 280$ ppm) of the modern atmosphere, but the principal incondensable greenhouse gas. Since the

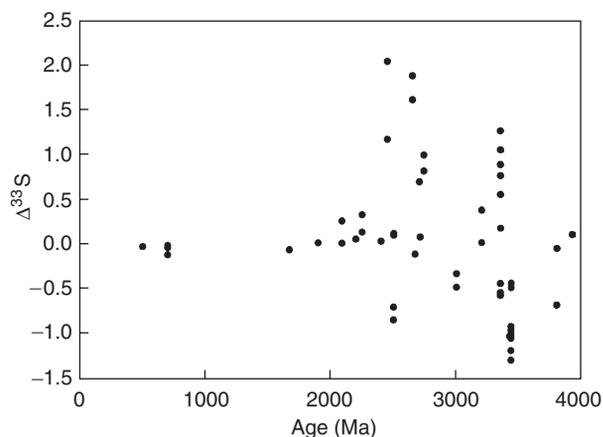


Figure 2 Evidence for a change in the sulfur cycle 2.5 billion years ago: the quantity $\Delta^{33}\text{S}$ is the deviation of $\delta^{33}\text{S}$ (the fractionation of the isotopes ^{33}S and ^{32}S with respect to a standard sample) away from a mass-dependent fractionation curve which relates $\delta^{33}\text{S}$ to $\delta^{34}\text{S}$ by a line with slope ~ 0.51 . All known biological and geochemical fractionation processes are mass-dependent, and any samples experiencing only these effects would have $\Delta^{33}\text{S} = 0$. While all samples younger than 2 billion years have $\Delta^{33}\text{S} = 0$, older samples exhibit mass-independent fractionation which is suggestive of an important role for gas-phase (atmospheric) reactions. This fractionation may be a consequence of an anoxic Archean atmosphere and a lack of oxidative weathering of sulfide minerals. (From Farquhar J, Baoh H, and Thieme M (2000) Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289: 756–758. Reprinted with permission.)

amounts of CO_2 in the oceans and carbonate rocks are equivalent to 0.023 and 40 atmospheres, respectively, there is the potential for substantial evolution in atmospheric carbon dioxide levels! Higher CO_2 is suspected as one cause for a warmer climate during the Jurassic and Cretaceous periods. It has been suggested that there was a secular decrease in atmospheric CO_2 over time, with levels as high as 300 hpa during the early Archean. The rationale for this hypothesis is the observation that the temperature-sensitive weathering of silicate rocks, which produces calcium and magnesium cations and alkalinity, could have regulated the formation of carbonate rocks and sequestration of CO_2 from the atmosphere. The weathering process acts as a global thermostat: lower carbon dioxide levels would bring about lower temperatures, which would slow weathering and carbonate formation, allowing CO_2 levels to rise. Likewise, lower solar luminosity in the past would have been compensated by higher p_{CO_2} . Although the geochemical logic is compelling, there is actually little evidence to confirm or refute the hypothesis. Under low-oxygen conditions, high CO_2 concentrations would have favored the precipitation of minerals such as siderite (iron carbonate). Absence of siderite in some paleosols may place a constraint on atmospheric CO_2 (Figure 3).

The history of nitrogen, the primary but relatively inert component of the modern atmosphere, is even

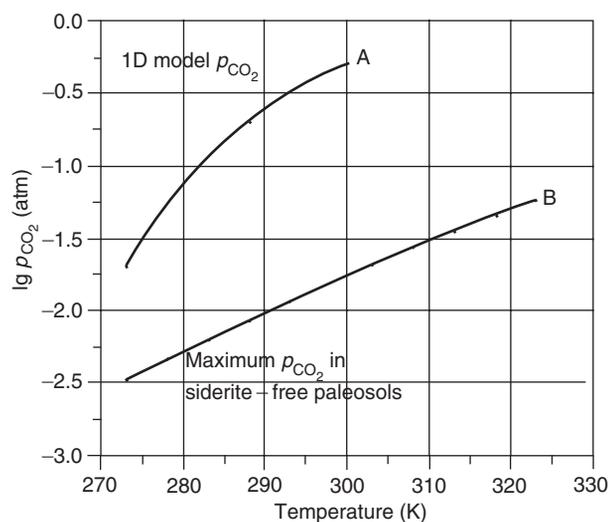


Figure 3 Geochemical constraints on atmospheric p_{CO_2} from the rock record. (A) Upper line, one-dimensional climate model prediction of p_{CO_2} as a function of global mean annual temperature at 2.75 Ga. (B) Lower line, estimate of the maximum p_{CO_2} in soil waters of siderite-free paleosols as a function of temperature. (From Rye R, Kuo PH, and Holland HD (1995) Atmospheric carbon-dioxide concentrations before 2.2 billion years ago. *Nature* 378: 603–605. Reprinted with permission.)

more poorly constrained by the geologic record. The relative abundance of the isotopes ^{15}N and ^{14}N in kerogens (organic molecules that are the sedimentary product of the breakdown of living organisms) in Precambrian rocks indicates a shift in relative abundance from lighter to heavier nitrogen during the late Archean. One explanation for the shift is an increase in the oxygen content of the atmosphere that led to an increased production in nitrate, either by atmospheric processes or by biology. Nitrate compounds are used by microorganisms, which either convert it to a reduced form (ammonia) to include eventually in cellular material, or use it as an oxidant in energy generation (denitrification). Reduction of nitrates by denitrifying bacteria yields isotopically light N_2 gas and isotopically heavy residual nitrates. As a result, surface nitrogen, including that in cells, becomes relatively heavy with respect to the atmosphere. The shift is small (about 10 ppm), and it is unlikely that there was a large change in the partitioning between the atmospheric reservoir (the largest) and surface nitrogen between the Archean and Proterozoic. Thus the nitrogen isotopes may be telling us more about the history of atmospheric oxygen than of nitrogen.

Atmospheric Evolution and the Gaia Hypothesis

According to accepted theories of the evolution of main sequence stars, of which the Sun is a typical member, the solar luminosity has been steadily increasing by about 40% since the Sun formed. The mean surface temperature of a planet like the Earth is determined by energy balance. If the composition of the atmosphere had remained unchanged, the Earth's mean surface temperature would have been below the freezing point of water before about 2 billion years ago. But the sedimentary record shows that liquid water has always been present on Earth. A plausible resolution of the 'faint young Sun' paradox is that the early atmosphere contained more greenhouse gases (e.g., CO_2). Two greenhouse gases other than CO_2 that have also been considered for this role are ammonia and methane. Both gases have strong absorption bands that fall within the spectral wavelength range or 'window' where the Earth reradiates most of the solar energy it receives back to space, but outside the primary CO_2 absorption band at $15\ \mu\text{m}$. Their abundances (mixing ratios) in the atmosphere will depend on their rates of production and destruction. The largest present-day sources of methane and ammonia are biological, and that is likely to have been the case at early times as well. While ammonia is a very effective

absorber of infrared radiation, it is easily destroyed by UV radiation and is unlikely to have been abundant enough in the Archean atmosphere. Methane, on the other hand, has a chemical lifetime of 10 years: CH₄ is stable with respect to molecular oxygen, but reaction with hydroxyl radicals (OH) from the photolysis of water vapor produces CH₃, which does readily react with O₂. In the absence of oxygen to remove the hydrogen also produced by photolysis, the OH can recombine with H and is no longer an effective sink for methane. The modern production rate can maintain a CH₄ mixing ratio of 10⁻³ in an anoxic atmosphere, a level that can act in concert with a modest amount of atmospheric CO₂ to maintain Archean temperatures above freezing. However, the dominant modern source of methane is the microbiota in the anoxic guts of termites and ruminants. It is not clear what the production rates would be in the Precambrian before animals existed.

It has been suggested that the existence and evolution of life on this planet may have had a profound impact on the climate by regulating the amounts of CO₂ and other greenhouse molecules in the atmosphere, or by controlling the production of aerosols and thereby modulating cloud formation. Observations of the fundamental role of biology in the cycling of atmospheric gases is one basis for the 'Gaia' hypothesis in which the biosphere is conceived as regulating climate to maintain suitable conditions for biological activity. The ability of the biosphere to maintain a global environment that is optimal for life is known as homeorhesis. That the terrestrial atmosphere has been subject to homeorhesis by the biosphere throughout its long history is an intriguing hypothesis but difficult to prove. Investigations into the evolution of Earth's atmosphere not only grapple with profound questions about our planet's habitability but also address the possible existence and detection of habitable planets and life around other stars. Human society, through the rapid combustion of buried organic compounds (fossil fuels), deforestation, and modulation of the planetary albedo, now influences the evolution of the atmosphere and climate. What kind of feedback role we will ultimately play in the continuing evolution of our planet's atmosphere and climate remains to be seen.

See also

Aerosols: Observations and Measurements; Role in Radiative Transfer. **Biogeochemical Cycles:** Carbon Cycle; Nitrogen Cycle. **Carbon Dioxide.** **Climate:** Overview. **Gaia Hypothesis.** **Global Change:** Human Impact of Climate Change; Upper Atmospheric Change. **Paleoclimatology:** Ice Cores; Varves. **Reflectance and Albedo, Surface.** **Thermosphere.** **Volcanoes:** Role in Climate.

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