Earth's Early Atmosphere

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Matthews, Eds., *Mars* (Univ. of Arizona Press, 1992); see especially R. O. Pepin and M. H. Carr, in *ibid.*, chap. 4; T. Owen, in *ibid.*, chap. 25.
7. J. F. Kasting, *Icarus* **94**, 1 (1991).
8. M. H. Carr, *ibid.* **68**, 187 (1986).
9. Y. L. Yung *et al.*, *ibid.* **76**, 146 (1989).
10. R. O. Pepin, *ibid.* **92**, 2 (1991).
11. J. Geiss and H. Reeves, *Astron. Astrophys.* **93**, 189 (1981); J. L. Linsky *et al.*, *Astrophys. J.* **402**, 694 (1993).
12. D. H. Grinspoon and J. S. Lewis, *Icarus* **74**, 21 (1988). The plausibility of a steady state depends on the fractionation factor, which is the relative efficiency of escape for H and D and must be the reciprocal of the enrichment factor. A recent evaluation by M. Gurwell and Y. L. Yung [*Bull Am. Astron. Soc.* **23**, 1194 (1991)] finds a much lower value than previously suggested and does not support a steady state with cometary water having the composition of Halley.
13. D. M. Hunten, T. M. Donahue, J. C. G. Walker, J. F. Kasting, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1989); D. M. Hunten and T. M. Donahue, *Annu. Rev. Earth Planet. Sci.* **4**, 265 (1976).
14. J. W. Chamberlain and D. M. Hunten, *Theory of Planetary Atmospheres* (Academic Press, Orlando, 1987).
15. T. M. Donahue, *Icarus* **66**, 195 (1986).
16. D. M. Hunten, *Geophys. Res. Lett.* **12**, 271 (1985); K. J. Zahnle and J. F. Kasting, *Icarus* **68**, 462 (1986); D. M. Hunten, R. O. Pepin, J. C. G. Walker, *ibid.* **69**, 532 (1987).
17. C. Sagan and G. Mullen, *Science* **177**, 52 (1972).
18. A. I. Boothroyd, I.-J. Sackmann, W. A. Fowler, *Astrophys. J.* **377**, 318 (1991); T. E. Graedel, I.-J. Sackmann, A. I. Boothroyd, *Geophys. Res. Lett.* **18**, 1881 (1991).
19. H. J. Melosh and A. M. Vickery, *Nature* **338**, 487 (1989).
20. W. Benz, W. L. Slattery, A. G. W. Cameron, *Icarus* **74**, 516 (1988); A. G. W. Cameron, B. Fegley, Jr., W. Benz, W. L. Slattery, in *Mercury*, F. Vilas, C. R. Chapman, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson), pp. 692–708.
21. T. Owen, A. Bar-Nun, I. Kleinfeld, *Nature* **358**, 43 (1992).
22. A. P. Ingersoll, *J. Atmos. Sci.* **26**, 1191 (1969); J. F. Kasting, *Icarus* **74**, 472 (1988).
23. D. M. Hunten, *Planet. Space Sci.* **30**, 773 (1982).
24. J. G. Luhmann and J. U. Kozyra, *J. Geophys. Res.* **96**, 5457 (1991); J. G. Luhmann and S. J. Bauer, in *Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions*, J. G. Luhmann, M. Tatrallyay, R. O. Pepin, Eds. (American Geophysical Union, Washington, DC, 1992), p. 417; J. G. Luhmann, R. E. Johnson, M. H. G. Zhang, *Geophys. Res. Lett.* **19**, 2155 (1992).
25. D. M. Hunten, *J. Atmos. Sci.* **30**, 1481 (1973).
26. T. Matsui and Y. Abe, *Earth Moon Planets* **34**, 207 (1986); M. A. Lange and T. J. Ahrens, *Icarus* **51**, 96 (1982); T. J. Ahrens, J. D. O'Keefe, M. A. Lange, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. S. Matthews Eds. (Univ. of Arizona Press, Tucson, 1989), pp. 328–385.
27. S. Kumar, D. M. Hunten, J. B. Pollack, *Icarus* **55**, 369 (1983). A correction by V. A. Krasnopolsky, [*ibid.* **62**, 221 (1985)] changes some details but not the general results.
28. J. F. Kasting and J. B. Pollack, *Icarus* **53**, 470 (1983).
29. See special Magellan issues, R. S. Saunders, Ed., *J. Geophys. Res.* **97** (1992), *ibid.*, pp. 13,059 and 15,921.
30. M. B. McElroy, *Science* **175**, 443 (1972); _____ and T. M. Donahue, *ibid.* **177**, 986 (1972); S. C. Liu and T. M. Donahue, *Icarus* **28**, 231 (1976).
31. T. Owen, J. P. Maillard, C. de Bergh, B. L. Lutz, *Science* **240**, 1767 (1988). G. L. Bjoraker, M. J. Mumma, and H. P. Larson [*Bull. Am. Astron. Soc.* **21**, 991 (1989)] report a small isotope effect in the oxygen of atmospheric water vapor in which the heavier isotopes are depleted rather than en-

riched. H. R. Karlsson, R. N. Clayton, E. K. Gibson, Jr., and T. K. Mayeda [*Science* **255**, 1409 (1992)] show that there are reservoirs of water in SNC meteorites that are not in isotopic equilibrium with each other.
32. A. O. Nier, M. B. McElroy, Y. L. Yung, *Science* **194**, 68 (1976); M. B. McElroy, T. Y. Kong, Y. L. Yung, *J. Geophys. Res.* **82**, 4379 (1977).
33. J. L. Fox and A. Dalgarno, *Planet. Space Sci.* **28**, 41 (1980); *J. Geophys. Res.* **88**, 9027 (1983); J. L. Fox, in *Dissociative Recombination: Theory, Experiment and Applications*, J. B. A. Mitchell and F. L. Guberman, Eds. (World Scientific, Singapore, 1989), pp. 264–285; M. K. Wallis, *Earth Planet. Sci. Lett.* **93**, 321 (1989).
34. R. Kahn, *Icarus* **62**, 175 (1985).
35. V. R. Baker *et al.*, *Nature* **352**, 589 (1991).
36. A. L. Broadfoot, S. Kumar, M. J. S. Belton, M. B. McElroy, *Science* **185**, 166 (1974); A. L. Broadfoot, D. E. Shemansky, S. Kumar, *Geo-*

phys. Res. Lett. **3**, 577 (1976).
37. R. R. Hodges, Jr., J. H. Hoffman, F. S. Johnson, *Icarus* **21**, 415 (1974); R. R. Hodges, Jr., *Moon* **14**, 139 (1975); W. G. Fastie, P. D. Feldman, R. C. Henry, H. W. Moos, T. M. Donahue, *Science* **182**, 710 (1973).
38 A. E. Potter and T. H. Morgan, *Science* **229**, 651 (1985), *Icarus* **67**, 336 (1986); D. M. Hunten, T. H. Morgan, D. E. Shemansky, in *Mercury*, F. Vilas, C. R. Chapman, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1988), pp. 562–612.
39. A. E. Potter and T. H. Morgan, *Science* **241**, 675 (1988); A. L. Tyler, R. W. H. Kozlowski, D. M. Hunten, *Geophys. Res. Lett.* **15**, 1141 (1988); A. L. Sprague, R. W. H. Kozlowski, D. M. Hunten, W. K. Wells, F. A. Grosse, *Icarus* **96**, 27 (1992).
40. I acknowledge valuable comments by T. M. Donahue, B. M. Jakosky, J. F. Kasting, T. C. Owen, A. L. Sprague, Y. L. Yung, and K. J Zahnle.

Earth's Early Atmosphere

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Ideas about atmospheric composition and climate on the early Earth have evolved considerably over the last 30 years, but many uncertainties still remain. It is generally agreed that the atmosphere contained little or no free oxygen initially and that oxygen concentrations increased markedly near 2.0 billion years ago, but the precise timing of and reasons for its rise remain unexplained. Likewise, it is usually conceded that the atmospheric greenhouse effect must have been higher in the past to offset reduced solar luminosity, but the levels of atmospheric carbon dioxide and other greenhouse gases required remain speculative. A better understanding of past atmospheric evolution is important to understanding the evolution of life and to predicting whether Earth-like planets might exist elsewhere in the galaxy.

A review paper on the subject of Earth's early atmosphere must, of necessity, be incomplete. A book, or perhaps several books, would be required to do justice to the topic. Here, I focus on four particular subtopics: formation of the atmosphere and ocean, the prebiotic atmosphere, long-term climate evolution, and the rise of O_2 levels. Each of these subtopics has seen an influx of new ideas over the past several years, although it would be presumptuous to claim that any of them are well understood as a result. To further limit the scope of this review, I restrict my discussion to the Precambrian Era, that is, the period before ~540 million years ago. Fluctuations in atmospheric CO_2 and O_2 levels have almost certainly occurred since that time (1), but these are second-order perturbations by comparison to the changes that took place earlier.

Formation of the Atmosphere and Ocean

Theories for how the atmosphere and ocean formed must begin with an idea of how the Earth itself originated. We are now reason-

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ably certain that the terrestrial planets formed by accretion of solid materials that condensed from the solar nebula (2). Any primary, captured atmosphere (if one existed at all) must have been lost, as evidenced by the pronounced depletion of rare gases in Earth's atmosphere compared to cosmic abundances (3). The present, secondary atmosphere was generated from volatile compounds contained within the solid planetesimals from which the Earth formed. Thirty years ago, it was believed that the Earth formed relatively slowly, with a cold interior, and that most of its volatiles were originally trapped inside the planet (4, 5). As time passed, the Earth's interior was heated by radioactive decay, and the trapped gases were gradually released by volcanic outgassing. These volcanic gases would have been highly reduced [containing H_2, methane (CH_4), and ammonia (NH_3)] until the Earth's core formed, after which time they would have been similar to modern volcanic gases (containing H_2O, CO_2, and N_2, with traces of H_2 and CO) (5).

More recent models of planetary accretion (6–8) suggest that the Earth formed in 10 to 100 million years and that its interior was initially hot as a consequence of large impact events, including one that may have formed the moon [see papers in (9)]. The

Earth's core probably formed simultaneously with accretion (10, 11); thus, metallic iron could have been removed from the upper mantle, and volcanic gases could have been relatively oxidized starting as early as 4.5 billion years ago (Ga) (12, 13). Moreover, many of Earth's volatiles were probably released on impact (14), and this process may have formed a transient steam atmosphere during at least part of the accretionary period (15). Indirect evidence for the presence of such an atmosphere is provided by the isotopic composition of rare gases in Earth's atmosphere, some of which appear to have been mass fractionated by rapid, hydrodynamic escape of hydrogen (16). (Escaping hydrogen can drag other gases with it; the lighter isotopes are carried off more easily than the heavy ones.) Other mechanisms have been proposed to explain the abundances of xenon isotopes (17), but the high $^{22}Ne/^{20}Ne$ ratio in the atmosphere [which exceeds that in both the solar wind and the mantle (18)] is hard to explain in any other manner (19). Hydrodynamic escape becomes difficult in the postaccretionary period (after ~4.5 Ga) because the solar extreme ultraviolet (EUV) flux would have been lower (20) and the energy available to fuel the escape process would have been reduced (21). Furthermore, the escape rate would have become limited by diffusion once H_2 became a minor component of the atmosphere (22, 23). H_2 would have been a major component of an accretionary, steam atmosphere as a consequence of reduction of water by infalling, metallic iron–rich planetesimals (24).

Once the main accretionary phase had ended, the surface heat flux would have dwindled, and the steam atmosphere would have rained out to form an ocean (25). The remaining atmosphere would probably have been dominated by carbon and nitrogen compounds, primarily CO_2, CO, and N_2 (26–28). Next to water, carbon is the most abundant volatile at the Earth's surface. Most of it is in the relatively nonvolatile form of carbonate rocks (limestone and dolomite). The estimated crustal abundance of carbon, ~10^{23} g (29), would be sufficient to produce a partial pressure of 60 to 80 bars, were all of it present in the atmosphere as CO_2. As much as 15% of this carbon may have resided in the atmosphere before the continents began to grow and carbonate rocks began to accumulate (27). Thus, a primitive atmosphere containing 10 bars of CO_2 + CO, along with approximately 1 bar of N_2, is possible during the first several hundred million years of Earth history. Climate modeling indicates that the mean surface temperature of such an atmosphere would have been ~85°C (30). Despite its warmth, such an atmosphere would be stable against runaway evaporation and
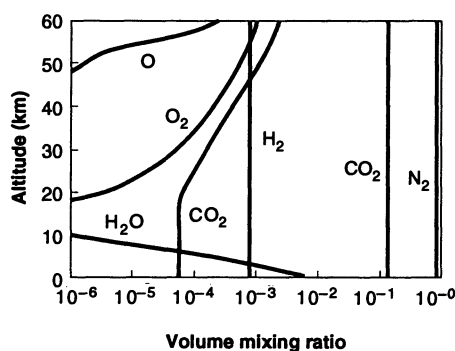

Volume mixing ratio

Fig. 1. Altitude profiles of major atmospheric constituents in a typical, weakly reduced, prebiotic atmosphere. The assumed volcanic outgassing rate of (H_2 + CO) is 2.6×10^{10} cm^{-2} s^{-1}, and hydrogen escapes to space at the diffusion-limited rate. [From (28)]

against loss of water by photodissociation and hydrogen escape.

Even after the main accretion phase had ended, Earth's surface environment would still have experienced rapid changes. The lunar cratering record indicates that significant numbers of large (100-km diameter) impactors continued to hit the Earth-moon system until at least 3.8 Ga. If some of these impactors were of cometary or carbonaceous chondritic composition, substantial amounts of water could have been brought in during this "heavy bombardment" period, from 4.5 to 3.8 Ga (31). The impacts could also have affected atmospheric composition by providing a source of CO and NO. CO would have been produced by oxidation of organic C in carbonaceous impactors or by reduction of ambient, atmospheric CO_2 by iron-rich impactors (28). NO would have been generated by shock heating of atmospheric CO_2 and N_2 (28, 32, 33). CO could potentially have reached high concentrations in the atmosphere, depending on its rate of hydration and disproportionation in the ocean (28). Such aqueous-phase reactions of CO need further study if we are to understand the composition of the atmosphere during this time period.

The Atmosphere at the Time of the Origin of Life

The heavy bombardment ended about 3.8 Ga; life was probably extant by 3.5 Ga, as evidenced by the presence of microfossils and stromatolites in ancient sediments (34, 35). The relatively narrow window of time between these two dates is the most probable time for life to have originated (36). Before 3.8 Ga, the uppermost layers of the ocean would probably have been repeatedly vaporized by large impacts (37, 38). Impactors exceeding 440 km in diameter could have vaporized the entire ocean, sterilizing

the planet with the possible exception of bacteria living in sediments or submarine hydrothermal systems. Events of this magnitude are possible before 3.8 Ga and probable before ~4.2 Ga (37). Thus, although life could have originated many times during the first part of Earth's history, it would probably not have survived until toward the end of the heavy bombardment.

One would like to know what the atmosphere consisted of around 3.8 Ga because the atmosphere plays a major role in at least some theories of the origin of life. Forty years ago, the Miller-Urey experiment (39) showed that many biologically important organic compounds, including sugars and amino acids, could be formed by spark discharge (simulating lightning) in a CH_4-NH_3-H_2-H_2O atmosphere. Subsequent reactions between these compounds could, in principle, have led to life's origin. However, CH_4 and NH_3 may not have been present in the atmosphere of early Earth. Modern volcanic gases are relatively oxidized: the major C gas released is CO_2; the major nitrogen gas is probably N_2 (26). Modern volcanic gases are in approximate equilibrium with magmas that have O_2 fugacities of the order of 10^{-9} MPa at 1200°C, close to the QFM (quartz-fayalite-magnetite) O_2 buffer (26). In order for CH_4 and NH_3 to become significant components of volcanic gases, the O_2 fugacity of the erupting magma would have to have been several orders of magnitude lower. So, whether CH_4 and NH_3 were present in the primitive atmosphere may depend on whether the oxidation state of the upper mantle has varied over time (40).

The question of whether the mantle oxidation state has changed is a difficult one because igneous rocks are rapidly oxidized once they are formed. Thus, whereas fresh midocean ridge basaltic glasses may retain their initial Fe^{+3}/Fe^{+2} ratios (41), older basalts are more oxidized. The approximate constancy of the Fe^{+3}/Fe^{+2} ratio of basalts and komatiites, which has been used by some to argue for a uniform mantle oxidation state throughout geologic time (5, 42), is therefore not a good indicator of how the mantle has evolved. This argument may have been supplanted by one based on the Cr content of basalts (43), which gives the same result, but the question is far from closed. Data from diamond inclusions indicate that at least parts of the upper mantle were once more reduced (13, 44). The mantle could have been oxidized gradually by recycling of water from the surface followed by volcanic outgassing of hydrogen (13). This process could have required hundreds of millions to billions of years to bring the mantle to its present oxidation state. It is thus premature to rule out a volcanic source of highly reduced gases at the time of life's origin (45, 46).

In the absence of a volcanic source of

methane and ammonia, the post–heavy bombardment atmosphere was probably dominated by CO_2 and N_2, with traces of CO, H_2, and reduced sulfur gases (23, 28, 47–49). This type of atmospheric composition is often termed "weakly reduced" (Fig. 1). The H_2 mixing ratio is fixed by the balance between the emission of reduced gases from volcanos and from the surface ocean, escape of hydrogen to space, and rainout of oxidized or reduced species (28). The H_2 level adjusts itself so that the overall redox balance of the atmosphere is maintained. The O_2 mixing ratio reaches ~0.1% at high altitudes, where it is produced from photodissociation of CO_2. O_2 is exceedingly rare near the surface [$<10^{-12}$ times the present atmospheric level (PAL)] because there is an excess of H_2 and because the reaction between these two gases is catalyzed by the by-products of water vapor photolysis.

With regards to the origin of life, the key question is whether photochemical reactions in such an atmosphere could have generated formaldehyde (H_2CO) and hydrogen cyanide (HCN). The former is needed for synthesis of sugars, the latter for synthesis of amino acids and nucleotides. Pinto et al. (48) demonstrated that an efficient pathway for formaldehyde synthesis exists even in a CO_2-dominated atmosphere; thus, this molecule should have been readily available. Formation of HCN is much more difficult because it requires breaking both an N≡N and a C≡O triple bond (if one starts from N_2 and CO_2). Both bonds can be severed in the high-temperature core of lightning discharges, but the resulting N and C atoms are more likely to combine with O atoms than with each other unless the atmospheric C:O ratio exceeds unity (32). Zahnle (46) has shown that HCN could be formed by ionospherically produced N atoms reacting with the photolysis by-products of trace amounts (1 to 10 ppm) of CH_4; however, such a scenario still requires a source for CH_4. Explaining how HCN could have formed is currently one of the major hurdles for theories of the origin of life that rely on the atmosphere as the source of starting materials. This difficulty has helped to spawn alternative theories in which the biological precursor molecules are brought in by impacting comets or other planetesimals (50) or are synthesized within submarine hydrothermal vents (51, 52).

Long-Term Climate Evolution

The typical, weakly reduced atmosphere shown in Fig. 1 contains 0.2 bar of CO_2, or roughly 600 PAL. The reason is that high concentrations of CO_2 or other greenhouse gases are probably needed to compensate for

Fig. 2. Atmospheric CO_2 concentrations required to compensate for reduced solar luminosity in the past, assuming no change in surface or cloud albedo. The 10-bar upper limit at 4.5 Ga is from Walker's model (27) of an ocean-covered Earth. CO_2 levels during the glacial periods at 2.5 Ga and 0.8 Ga were calculated with a radiative-convective climate model, with the assumption that the mean surface temperature was between 5° and 20°C. (The current mean surface temperature is 15°C.) CO_2 concentrations at other times were estimated by stipulating that the Earth remain ice-free throughout most of the Precambrian. [After (62, 63)]
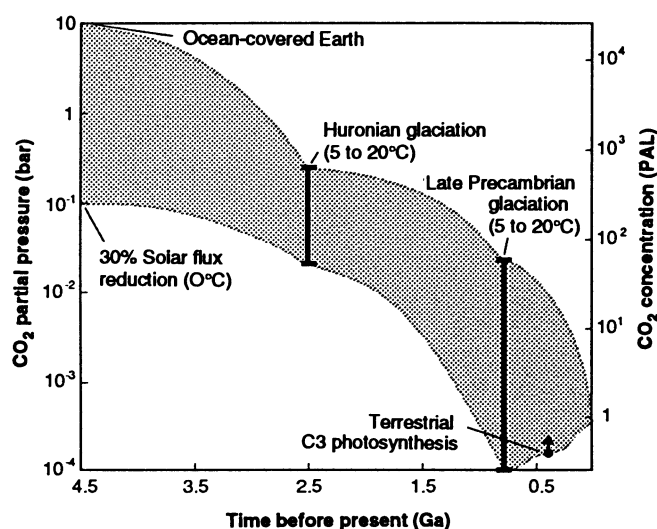
a predicted reduction in solar luminosity of ~30% at 4.6 Ga (53). If the composition of the atmosphere had remained unchanged, Earth's mean surface temperature should have been below the freezing point of water before ~2 Ga (54, 55). Global glaciation would have been the likely result. But we know from the formation of sedimentary rocks at 3.8 Ga and the presence of life from 3.5 Ga onward that liquid water existed on Earth's surface early in its history (54–56). This problem has been termed the "faint young sun" paradox. It is only a paradox, however, if one assumes that the composition of Earth's atmosphere has remained constant.

The faint young sun problem can be solved if either the Earth's albedo was lower in the past or the atmospheric greenhouse effect was larger (57). Some authors (58) have suggested that the albedo was lower because of decreased cloud cover on a colder planet. This solution is unlikely because the early Earth appears to have been, if anything, warmer than it is today. The earliest firm evidence for glaciation occurs at 2.3 to 2.5 Ga (59, 60). The geologic record is admittedly sparse during the Archean Era (2.5 to 3.8 Ga), so the absence of glaciation could be an artifact of preservation; however, there are theoretical reasons as well to expect a warm early Earth (see discussion above).

A more likely solution to the faint young sun problem is the presence of enhanced concentrations of greenhouse gases in Earth's early atmosphere. CO_2 is the most likely candidate (55, 56, 61, 62). A negative feedback mechanism involving changes in the rate of CO_2 consumption by silicate weathering could account for high CO_2 levels in the past (61). The argument
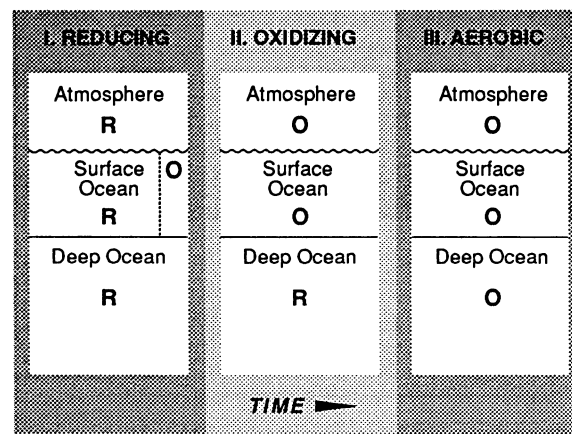
goes as follows: If other factors affecting climate did not change, a dimmer sun would have led to colder surface temperatures. This, in turn, would have decreased the silicate weathering rate and caused volcanically emitted CO_2 to accumulate in the atmosphere. Higher atmospheric CO_2 levels would have increased the greenhouse effect and thus warmed the climate. Atmospheric CO_2 concentrations should have risen to whatever level was needed to keep the oceans from freezing and to balance the global C budget.

To accomplish this, the atmospheric CO_2 concentration must have declined from >300 PAL at 4.6 Ga to ~1 to 10 PAL near the end of the Proterozoic (0.6 Ga) (Fig. 2) (63). This calculation assumes that CO_2 and water vapor were the only important greenhouse gases and that changes in cloudiness can be neglected. The first assumption is discussed below; the second appears to be bold, but may be justified for periods when the mean surface temperature was close to its present value, which must have happened at least occasionally during this time interval. These predictions are entirely theoretical: There are no reliable paleo-CO_2 indicators that would allow them to be tested empirically. Declining atmospheric CO_2 concentrations over the past 2.5 Ga are, however, qualitatively consistent with the observed increase in the $^{13}C/^{12}C$ ratio of marine kerogens (64).

The assumption that other greenhouse gases were absent is probably valid for only part of geologic time. Methane and ammonia are both good greenhouse gases that could have helped compensate for reduced solar luminosity (54, 65). As discussed earlier, there is no obvious large source for these gases before the origin of life. Once

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Fig. 3. Three-box model for the rise of atmospheric oxygen. O, oxidizing conditions; R, reducing conditions. The small box in the surface ocean during stage I represents a local oxygen oasis.

I. REDUCING	II. OXIDIZING	III. AEROBIC
Atmosphere R	Atmosphere O	Atmosphere O
Surface Ocean R / O	Surface Ocean O	Surface Ocean O
Deep Ocean R	Deep Ocean R	Deep Ocean O

TIME ➤

life had originated, however, both gases should have been produced by anaerobic decay processes, and CH_4 would have been generated directly by methanogenic bacteria that metabolized CO_2 and H_2 (23). Thus, during the Archean, the atmospheric greenhouse effect may have been augmented by methane and ammonia, in which case CO_2 levels could have been lower than shown in Fig. 2. Once atmospheric O_2 became abundant around 2.0 Ga (see next section), the concentrations of reduced gases would have fallen dramatically (62), so CO_2 and H_2O were probably the main greenhouse constituents.

The biggest controversy concerning long-term climate regulation has to do with the effect of the biota. Some authors (66, 67) have suggested that the biota play an integral role in controlling atmospheric CO_2. They do so primarily by pumping up the CO_2 partial pressure in soils and by generating humic acids, both of which accelerate the rate of CO_2 removal by weathering. One analysis (67) suggested that if life were absent, the current CO_2 partial pressure would have been several tenths of a bar and the mean surface temperature would have been 60°C warmer than it is today. A more conservative analysis based on soil CO_2 levels alone (68) suggests that the biotic drawdown of surface temperature is much smaller (~6°C rather than 60°C); nevertheless, it is apparent that the biota probably do influence Earth's climate.

The Rise of Oxygen and Ozone

The most obvious consequence of biological activity is the high O_2 partial pressure in the present atmosphere. It has been long recognized that photosynthesis, followed by burial of organic carbon (69), is the source of most of our O_2. The amount of free O_2 that can be produced abiotically by photodissociation of H_2O followed by escape of H to space is small (23, 49). Photodissociation of water vapor might produce large

amounts of O_2 on a planet that experienced a runaway greenhouse (70), but these conditions were not encountered on early Earth (30). (The accretionary steam atmosphere is a type of runaway greenhouse, but it would likely have been kept O_2-free by the infall of reduced material.)

The question of when atmospheric O_2 levels rose can be addressed by examining the geologic record. The first systematic attempt to do so was made by Cloud (71). He observed that redbeds (oxidized subaerial deposits) were absent before about 2 Ga and that deposits of detrital pyrite and uraninite were mostly formed before this time. These minerals are usually oxidized during weathering under the high partial pressure of O_2 of today's atmosphere. Furthermore, banded iron formations (BIFs) were formed up until ~1.85 Ga (72), but not after (73, 74). Deposition of BIFs is thought to require an anoxic deep ocean so that iron can be transported long distances

in its soluble ferrous form (75). These factors, taken together, led Cloud to propose that atmospheric O_2 first rose to appreciable levels at about 2 Ga.

Most recent analyses of the rise of O_2 levels are in general agreement with the model proposed by Cloud. Holland (76) placed the time of major increase in levels of O_2 at between 2.2 and 1.9 Ga on the basis of a variety of types of geologic evidence, including the analysis of paleosols (ancient soils). Walker *et al.* (77) described an elaboration of Cloud's model in which O_2 levels rose in four separate stages: a reducing stage, two oxidizing stages, and an aerobic stage. Kasting (62) showed that one of the oxidizing stages could be eliminated and proposed the three-stage model shown in Fig. 3. This model could also be termed a "three-box" model because the atmosphere, surface ocean, and deep ocean constitute three distinct reservoirs for O_2. In stage I, the atmosphere and the entire ocean were anoxic, with the possible exception of localized oxygen oases in highly productive regions of the surface ocean (78). In stage II, the atmosphere and surface ocean were oxidizing, whereas the deep ocean remained anoxic. The need for this stage is dictated by the possible overlap between the redbed record and the BIF record (79). In stage III, both the atmosphere and ocean contained abundant free O_2, as on the modern Earth.

Some theoretical estimates for atmospheric O_2 levels may be drawn from considerations of mass balance in the three-box model. The O_2 concentration during stage II could not have exceeded ~0.03 PAL because O_2 that downwelled into the deep ocean would have been lost faster than it was

Fig. 4. Estimated change in atmospheric O_2 levels over geologic time. The shaded area represents the range of O_2 concentrations permitted by the data. The solid vertical lines represent the most likely dates for the transitions between stages. The dashed vertical line at 2.4 Ga indicates a possible earlier date for the beginning of stage II that is consistent with some disputed redbed data (77) and with the early appearance of *Grypania*. The dashed horizontal lines show the theoretical limits on the partial pressure of O_2 (pO_2) derived from the three-box model. The upper limit on Archean pO_2 from uraninite survival is derived from equation 7.30 of (26) for CO_2 partial pressures from Fig. 2. The point labeled "Kuruman BIF" is a lower limit on pO_2 based on a paleoweathering rate analysis (81). The lower limits on Late Proterozoic and Phanerozoic pO_2 labeled "Dickinsonia" and "Charcoal" are from (83) and (84), respectively. The arrow labeled "Abundant Phytoplankton" is from (34). Other constraints on pO_2 are described in the text.
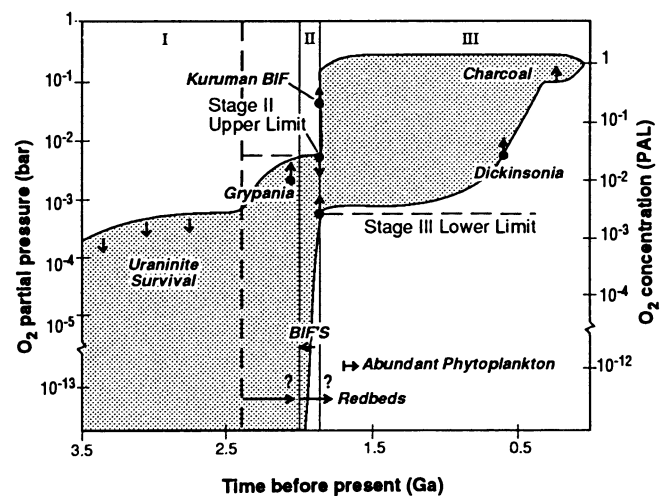
being produced (62). The O_2 concentration during stage III could not have been less than 0.002 PAL (78) because the deep ocean would have remained anoxic as a consequence of the influx of reductants from hydrothermal vents. Both limits are for the assumption that deep ocean circulation rates then were similar to those of today, and the first limit also is for a modern rate of organic carbon burial. Additional constraints can be imposed from analyses of detrital uraninites (26) and paleosols (80, 81) and from consideration of the fossil record (Fig. 4) (34, 79, 82–84). One recent change in Fig. 4 is that the first appearance of Grypania (a corkscrew-shaped organism, possibly a photosynthetic algae) has been pushed back to 2.1 Ga (85). What this implies about the rise of O_2 levels in the atmosphere is not clear. Eukaryotic organisms like Grypania probably require at least 0.01 PAL of dissolved O_2 in the water column to satisfy their metabolic requirements (83). This level is below the upper limit for stage II and could even have occurred during stage I. The upper limit for dissolved O_2 in localized oxygen oases is ~0.08 PAL (78). Thus, the existence of eukaryotic organisms at 2.1 Ga, and possibly earlier (85, 86), does not necessarily mean that the atmosphere contained free O_2.

Other workers have suggested that free O_2 was present in the atmosphere well before 2.0 Ga (87). Low $^{13}C/^{12}C$ ratios in 2.8 billion-year-old organic sediments imply that oxygenic photosynthesis had already originated by that time (88). The presence of stromatolites in 2.7-billion-year-old lacustrine (lakebed) sediments from the Tumbiana Formation in Western Australia supports this conclusion (89). Towe (90) has suggested that free O_2 must have been present during the Archean to create an ozone screen against solar ultraviolet radiation and to recycle the organic matter produced by photosynthesis. However, an Archean analog to the present ozone screen could have been provided by hydrocarbon particles produced from methane photolysis (91), and primary photosynthetic productivity may have been smaller than Towe assumed (79). The dispute over Archean O_2 levels might be resolved by a more detailed analysis of how much O_2 is required to form redbeds (49, 77, 79).

Even if one accepts the conclusion that free O_2 first appeared in the atmosphere at about 2 Ga, why it did so at this time remains a puzzle. Walker (92) suggested that the transition from a reducing to an oxidizing atmosphere, stage I to stage II in the model proposed above, occurred when the net rate of photosynthetic O_2 production exceeded the rate of consumption of O_2 by reaction with volcanic H_2. A declining volcanic outgassing rate could have

triggered this change. The transition from stage II to stage III could have been caused by an increase in carbon burial associated with increased continental shelf area (77, 93). Neither of these hypotheses, however, is consistent with the conventional interpretation of the carbon isotopic record (94), which asserts that the average isotopic composition of both carbonate and organic carbon in sedimentary rocks has remained essentially unchanged with time. If true, the fraction of outgassed CO_2 that was utilized in photosynthesis and buried as organic carbon would have necessarily remained constant at its present value of ~0.2 (94). As long as the ratio of H_2:CO_2 in volcanic gases did not change, any decline in H_2 outgassing would have been accompanied by a corresponding decline in organic carbon burial. So, the source for O_2 would decrease in direct proportion to its volcanic sink.

One way out of this dilemma would be for the H_2:CO_2 ratio in volcanic gases to decrease with time (13). Such a change could have occurred if the mantle oxidation state increased with time as a consequence of recycling of ocean water and the outgassing of H_2 and other reduced gases. As discussed earlier, recent evidence (43) suggests that this was not the case, but the question deserves further study. A second possibility is that the long-term carbon isotopic record is not as uniform as previously believed. DesMarais and co-workers (64) analyzed the isotopic composition of well-preserved marine kerogens (H:C ratio >0.2) and concluded that there is a trend: kerogen became isotopically heavier in two distinct steps between 2.5 and 2.0 Ga and again between 1.1 and 0.8 Ga (95). This increase in the $^{13}C/^{12}C$ ratio in kerogens translates to an overall increase in the organic carbon burial fraction from 0.1 to 0.2. If these data correctly reflect the overall isotopic composition of organic matter buried at that time, the rise in atmospheric O_2 levels near 2.0 Ga can be nicely explained. The problem then is to explain why the organic carbon burial fraction increased with time. DesMarais et al. attributed the change to episodes of increased continental rifting and orogeny. Alternatively, the increase in organic carbon burial between 2.5 and 2.0 Ga might be tied to a change in atmospheric oxidation state: If the atmosphere switched from reducing to oxidizing during this time, the amount of H escaping to space would have declined dramatically, allowing more of it to be utilized in reducing CO_2. Thus, it is not clear whether the change in the organic carbon burial rate was a cause or a consequence of the rise in atmospheric O_2.

Another factor that could have affected the rise of O_2 was the formation of the

ozone layer (62). Photochemical model calculations (62, 96) predict that a biologically effective ultraviolet screen would have been established at an O_2 concentration of 0.01 to 0.1 PAL. Before atmospheric O_2 concentrations reached this level, eukaryotic phytoplankton would have been excluded from the oceans because of their intolerance to high levels of ultraviolet radiation. The resulting decrease in marine productivity compared to today could have caused less organic carbon to be buried, as implied by the new isotopic data (64), or it could have necessitated a lower atmospheric O_2 level to maintain a constant organic carbon burial fraction (26, 97).

The final major episode in the rise of atmospheric O_2 levels may have occurred near the end of the Proterozoic, between 550 and 600 Ma. High $^{13}C/^{12}C$ ratios in marine carbonates formed at this time indicate a marked increase in the rate of organic C burial and, hence, in O_2 production (74, 98). This O_2 was evidently not utilized in oxidizing sulfide to sulfate, as evidenced by a lack of correlation between C and S isotopes (74). An increase in the $^{87}Sr/^{86}Sr$ isotope ratio of seawater and the cessation of BIF formation at this same time indicate that the O_2 sink from hydrothermal reductants was diminishing in magnitude (74); thus, some of the excess O_2 probably ended up in the atmosphere. A rise in atmospheric O_2 just before the emergence of multicellular organisms in the Ediacaran and their diversification during the Cambrian is consistent with long-held views about the importance of O_2 levels to biological evolution (86, 99).

Summary and Extensions

Although many of the details of how Earth's atmosphere evolved remain unresolved, a general picture has emerged. The formation of an atmosphere containing N_2 and CO_2 and an ocean containing H_2O appears to be a natural consequence of planetary accretion in the terrestrial planet region. The weakly reducing primitive atmosphere provided an environment conducive to the origin of life, regardless of whether the important biological precursor compounds were synthesized there or elsewhere. Atmospheric O_2 levels rose naturally, but not immediately, as a consequence of photosynthesis and organic carbon burial. At the same time, the concentrations of CO_2 and other greenhouse gases declined in such a way as to compensate for the brightening sun. Earth's relatively stable climate was probably a result of the negative feedback between atmospheric CO_2, surface temperature, and the weathering rate of silicate rocks.

These general conclusions about atmo-

spheric evolution imply that Earth may not be unique. If planets exist around other stars, as seems likely, at least some of them should reside in orbits where the illumination is comparable to that received by Earth. Buffering of planetary climates by the carbonate-silicate cycle implies that the habitable zone around late F to mid K stars may be reasonably wide, so that many such planets may exist (100). If the origin of life was not a fortuitous event, many of these planets could be inhabited and some may even have evolved intelligent life. Both of these speculations can be tested: the first by spectroscopic investigations from large, space-based telescopes (101), and the second by monitoring microwave and radio emissions from space (102). From an atmospheric scientist's standpoint, there is good reason to proceed with both of these searches.

REFERENCES AND NOTES

1. R. A. Berner, A. C. Lasaga, R. M. Garrels, *Am. J. Sci.* **283**, 641 (1983); A. C. Lasaga, R. A. Berner, R. M. Garrels, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*, E. T. Sundquist and W. S. Broecker, Eds. (American Geophysical Union, Washington, DC, 1985), pp. 397–411; R. A. Berner and D. E. Canfield, *Am. J. Sci.* **289**, 333 (1989); M. I. Budyko, A. B. Ronov, A. L. Yanshin, *History of the Earth's Atmosphere* (Springer-Verlag, Berlin, 1987); R. A. Berner, *Science* **249**, 1382 (1990).
2. V. S. Safronov, *NASA Rep. TT F-677* (1972).
3. B. Aston, *Nature* **114**, 786 (1924); H. Brown, in *The Atmospheres of the Earth and Planets*, G. P. Kuiper, Ed. (Univ. of Chicago Press, Chicago, 1952), pp. 258–266.
4. W. W. Rubey, *Geol. Soc. Am. Bull.* **62**, 1111 (1951).
5. H. D. Holland, in *Petrologic Studies: A Volume to Honor A. F. Buddington*, A. E. J. Engel, H. L. James, B. F. Leonard, Eds. (Geological Society of America, New York, 1962), pp. 447–477.
6. V. S. Safronov and T. V. Ruzmaikina, in *Protostars and Protoplanets II*, D. Black and M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1986), pp. 959–980.
7. G. W. Wetherill, *Science* **228**, 877 (1985).
8. _____, in (9), pp. 519–550.
9. W. K. Hartmann, R. J. Phillips, G. J. Taylor, *Origin of the Moon* (Lunar and Planetary Institute, Houston, TX, 1986).
10. D. J. Stevenson, in *Origin of the Earth*, H. E. Newsom and J. H. Jones, Eds. (Oxford Univ. Press, New York, 1990), pp. 231–249.
11. H. E. Newsom and K. W. W. Sims, *Science* **252**, 926 (1991).
12. The issue of whether the oxidation state of volcanic gases has remained constant is not yet resolved. See (13) and discussion below.
13. J. F. Kasting, D. H. Eggler, S. P. Raeburn, *J. Geol.*, in press.
14. A. Benlow and A. J. Meadows, *Astrophys. Space Sci.* **46**, 293 (1977); M. A. Lange and T. J. Ahrens, *Icarus* **51**, 96 (1982).
15. T. Matsui and Y. Abe, *Nature* **319**, 303 (1986); K. J. Zahnle, J. F. Kasting, J. B. Pollack, *Icarus* **74**, 62 (1988).
16. D. M. Hunten, *Science* **259**, 905 (1993).
17. M. Ozima and K. Nakazawa, *Nature* **284**, 313 (1980); K. J. Zahnle, J. B. Pollack, J. F. Kasting, *Geochim. Cosmochim. Acta* **54**, 2577 (1990).
18. M. Ozima and G. Igarashi, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1989), pp. 306–327.
19. K. Zahnle, J. F. Kasting, J. B. Pollack, *Icarus* **84**, 502 (1990).
20. V. M. Canuto, J. Levine, T. Augustsson, C. Imhoff, *Nature* **296**, 816 (1982); K. J. Zahnle and J. C. G. Walker, *Rev. Geophys. Space Phys.* **20**, 280 (1982).
21. It has been argued that solar EUV energy would have been blocked out by interplanetary dust during the main accretion period [R. G. Prinn and B. Fegley, Jr., in (18), pp. 78–136], but this may not have been true once the planetesimals had aggregated into relatively large bodies. This happens relatively early during accretion, according to Wetherill (8).
22. D. M. Hunten, *J. Atmos. Sci.* **30**, 1481 (1973).
23. J. C. G. Walker, *Evolution of the Atmosphere* (Macmillan, New York, 1977).
24. G. Dreibus and H. Wänke, in (18), pp. 268–288.
25. Actually, if impacts were large and sporadic, as suggested by Weatherill (7), the steam atmosphere may have condensed out and reevaporated several times.
26. H. D. Holland, *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, Princeton, NJ, 1984).
27. J. C. G. Walker, *Orig. Life* **16**, 117 (1985).
28. J. F. Kasting, *ibid.* **20**, 199 (1990).
29. A. B. Ronov and A. A. Yaroshevskiy, *Geochemistry* **11**, 1041 (1967); H. D. Holland, *The Chemistry of the Atmosphere and Oceans* (Wiley, New York, 1978).
30. J. F. Kasting and T. P. Ackerman, *Science* **234**, 1383 (1986).
31. E. Anders and T. Owen, *ibid.* **198**, 453 (1977); C. F. Chyba, *Nature* **330**, 632 (1987); *ibid.* **343**, 129 (1989).
32. W. L. Chameides and J. C. G. Walker, *Orig. Life* **11**, 291 (1981).
33. B. Fegley, R. G. Prinn, H. Hartman, G. H. Watkins, *Nature* **319**, 305 (1986).
34. J. W. Schopf, Ed., *Earth's Earliest Biosphere: Its Origin and Evolution* (Princeton Univ. Press, Princeton, NJ, 1983).
35. J. W. Schopf and B. M. Packer, *Science* **237**, 70 (1987).
36. K. A. Maher and D. J. Stevenson, *Nature* **331**, 612 (1988).
37. N. H. Sleep, K. J. Zahnle, J. F. Kasting, H. J. Morowitz, *ibid.* **342**, 139 (1989).
38. A 100-km-diameter impactor, equal in size to the ones that produced the craters Imbrium and Orientale on the Moon, would evaporate the top 30 m of the ocean (37). Impactors of twice this diameter would have vaporized the entire photic zone.
39. S. L. Miller, *Science* **117**, 528 (1953); _____ and H. C. Urey, *ibid.* **130**, 245 (1959).
40. D. Summers [paper presented at the 203rd ACS Meeting GEOC 149 (American Chemical Society, San Francisco, 1992)] has discovered a possible alternative source for ammonia involving formation of nitrate or nitrite in the atmosphere, followed by reaction with dissolved ferrous iron in the ocean.
41. D. M. Christie, I. S. E. Carmichael, C. H. Langmuir, *Earth Planet. Sci. Lett.* **79**, 397 (1986).
42. S. Chang, D. DesMarais, R. Mack, S. L. Miller, G. E. Strathearn, in (34), pp. 53–92.
43. J. Delano, personal communication.
44. D. H. Eggler, J. W. Harris, N. V. Sobolev, E. S. Yefimova, J. P. Lorand, in preparation.
45. Even if methane and ammonia were released from volcanos, they would have been minor atmospheric constituents because they are rapidly destroyed by photolysis [W. R. Kuhn and S. K. Atreya, *Icarus* **37**, 207 (1979); see also (46)]. But they could still have played an important role in the chemistry of life's origins.
46. K. J. Zahnle, *J. Geophys. Res.* **91**, 2819 (1986).
47. Y. L. Yung and M. B. McElroy, *Nature* **203**, 1002 (1979); J. S. Levine, *J. Mol. Evol.* **18**, 161 (1982).
48. J. P. Pinto, G. R. Gladstone, Y. L. Yung, *Science* **210**, 183 (1980).
49. J. F. Kasting and J. C. G. Walker, *J. Geophys. Res.* **86**, 1147 (1981).
50. J. Oro, *Nature* **190**, 389 (1961); C. F. Chyba, P. J. Thomas, L. Brookshaw, C. Sagan, *Science* **249**, 366 (1990).
51. J. B. Corliss, J. A. Baross, S. E. Hoffman, *Ocean Acta* **4** (suppl.), 59 (1981); E. L. Shock, *Orig. Life* **20**, 331 (1990).
52. Special issues dealing with the comet theory and the hydrothermal vent theory have been published recently as *Orig. Life* **21**, Nos. 5 and 6, (1991–1992) and *ibid.* **22**, Nos. 1 to 4 (1992).
53. M. J. Newman and R. T. Rood, *Science* **198**, 1035 (1977); D. O. Gough, *Sol. Phys.* **74**, 21 (1981); R. L. Gilliland, *Global Planet. Change* **1**, 35 (1989).
54. C. Sagan and G. Mullen, *Science* **177**, 52 (1972).
55. J. F. Kasting, O. B. Toon, J. B. Pollack, *Sci. Am.* **256**, 90 (February 1988).
56. T. Owen, R. D. Cess, V. Ramanathan, *Nature* **277**, 640 (1979).
57. The faint young sun problem could also be solved if the early sun was more massive than it is today [T. E. Graedel, I.-J. Sackmann, A. I. Boothroyd, *Geophys. Res. Lett.* **18**, 1881 (1991)], but such nonstandard solar models have yet to be accepted by the astronomical community.
58. A. Henderson-Sellers, *Nature* **279**, 786 (1979); W. B. Rossow, A. Henderson-Sellers, S. K. Weinreich, *Science* **217**, 1245 (1982).
59. L. A. Frakes, *Climates Throughout Geologic Time* (Elsevier, New York, 1979); T. J. Crowley, *Rev. Geophys. Space Phys.* **21**, 828 (1983).
60. A possible earlier glaciation recorded in the Witwatersrand sequence in South Africa is discussed by J. C. Crowell [*Trans. Geol. Soc. S. Afr.* **86**, 237 (1983)].
61. J. C. G. Walker, P. B. Hays, J. F. Kasting, *J. Geophys. Res.* **86**, 9776 (1981).
62. J. F. Kasting, *Precambrian Res.* **34**, 205 (1987).
63. _____, in *The Proterozoic Biosphere: A Multidisciplinary Study*, J. W. Schopf and C. Klein, Eds. (Cambridge Univ. Press, Cambridge, 1992), pp. 165–168.
64. D. J. DesMarais, H. Strauss, R. E. Summons, J. M. Hayes, *Nature* **359**, 605 (1992).
65. J. T. Kiehl and R. E. Dickinson, *J. Geophys. Res.* **92**, 2991 (1987).
66. J. E. Lovelock and M. Whitfield, *Nature* **296**, 561 (1982).
67. D. W. Schwartzman and T. Volk, *ibid.* **340**, 457 (1989).
68. J. F. Kasting and D. H. Grinspoon, in *The Sun in Time*, C. P. Sonett, M. S. Giampapa, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1991), pp. 447–462.
69. L. Van Valen, *Science* **171**, 439 (1971).
70. J. F. Kasting, *Icarus* **74**, 472 (1988).
71. P. E. Cloud, *Am. J. Sci.* **272**, 537 (1972), and references therein.
72. C. Klein and N. J. Beukes, in (63), pp. 139–146.
73. A few anomalous BIFs, including the Urucum in Brazil and the Rapitan in Canada, were formed much later near the end of the Proterozoic [see (72)]. Their possible significance is discussed in (74).
74. L. A. Derry, A. J. Kaufman, S. B. Jacobsen, *Geochim. Cosmochim. Acta* **56**, 1317 (1992).
75. H. D. Holland, *Econ. Geol.* **68**, 1169 (1973).
76. _____, in *Early Life on Earth (Nobel Symposium No. 84)*, S. Bengtson, Ed., in press.
77. J. C. G. Walker, C. Klein, M. Schidlowski, J. W. Schopf, D. J. Stevenson, M. R. Walter, in (34), pp. 260–290.
78. J. F. Kasting, in (63), pp. 1185–1187.
79. _____, *Glob. Planet. Change* **97**, 125 (1991).
80. H. D. Holland, C. R. Feakes, E. A. Zbinden, *Am. J. Sci.* **289**, 362 (1989).
81. H. D. Holland and N. J. Beukes, *ibid.* **290-A**, 1 (1990).
82. B. Runnegar, *Alcheringa* **6**, 223 (1982).
83. _____, *Glob. Planet. Change* **97**, 97 (1991).
84. T. P. Jones and W. G. Chaloner, *ibid.*, p. 39.
85. T.-M. Han and B. Runnegar, *Science* **257**, 232 (1992).
86. A. H. Knoll, *ibid.* **256**, 622 (1992).
87. A list of references relevant to this debate can be found in H. D. Holland, B. Lazar, M. McCaf-

frey, *Nature* **320**, 27 (1986).
88. J. M. Hayes, in (*34*), pp. 291–301.
89. R. Buick, *Science* **255**, 74 (1992).
90. K. M. Towe, *Precambrian Res.* **16**, 1 (1981); *ibid.* **20**, 161 (1983); *Nature* **348**, 54 (1990).
91. J. Lovelock, *The Ages of Gaia* (Norton, New York, 1988).
92. J. C. G. Walker, *Pure Appl. Geophys.* **117**, 498 (1978).
93. A. H. Knoll, *Orig. Life* **9**, 313 (1979).
94. M. Schidlowski, J. M. Hayes, I. R. Kaplan, in (*34*), pp. 149–186.
95. If DesMarais and co-workers are correct, the fractionation between carbonate and organic carbon has decreased with time. As pointed out earlier, this is consistent with a declining atmospheric CO_2 concentration. Photosynthetic organisms discriminate less strongly against the heavier carbon isotope when they are deprived of CO_2.
96. E. Hesstvedt, S. Henrikson, H. Hjartarson, *Geophys. Norv.* **31**, 1 (1974); A. J. Blake and J. H. Carver, *J. Atmos. Sci.* **34**, 720 (1977); J. S. Levine, P. B. Hays, J. C. G. Walker, *Icarus* **39**, 295 (1979); J. F. Kasting, H. D. Holland, J. P.

Pinto, *J. Geophys. Res.* **90**, 10,497 (1985).
97. This bootstrapping explanation for the rise of O_2 levels could therefore be viable regardless of one's interpretation of the C isotopic data.
98. High $^{13}C/^{12}C$ ratios occur also between 650 and 800 million years ago [A. H. Knoll, J. M. Hayes, A. J. Kaufman, K. Swett, I. B. Lambert, *Nature* **321**, 832 (1986)], but concurrently measured Sr isotope ratios imply that the organic carbon burial rate was low during this time. The isotope shift may have been caused by a temporary return to anoxic conditions in the deep ocean (*74*).
99. J. R. Nursall, *Nature* **183**, 1170 (1959); L. V. Berkner and L. C. Marshall, *J. Atmos. Sci.* **22**, 225 (1965).
100. J. F. Kasting, D. P. Whitmire, R. T. Reynolds, *Icarus*, in press.
101. *TOPS: Toward Other Planetary Systems* (NASA Solar System Exploration Division, Washington, DC, 1992).
102. This NASA project, formerly known as the Search for Extraterrestrial Intelligence (SETI), has been renamed the High Resolution Microwave Survey (HRMS).

levels predict a global warming between $\sim 2°$ and $5°C$ (*1*). The wide range of these predictions reflects mainly the uncertainties linked with cloud feedback (*2*).

In addition, there are a number of potential feedbacks on the CO_2, CH_4, and N_2O cycles when the climate is changing [see (*3*) for a review]. Thus, exchanges of atmospheric CO_2 with terrestrial ecosystems and the ocean are largely controlled by temperature and oceanic circulation. Likewise, CH_4 emissions from wetlands are particularly sensitive to temperature and soil moisture. These feedbacks are generally difficult to quantify.

There is another type of feedback that complicates the understanding of the greenhouse gas–climate system. It results from the complex atmospheric chemistry involved, and we term it "chemical feedback." One illustration is the oxidation of CH_4 by OH radicals producing stratospheric water vapor and tropospheric O_3, two other radiatively active gases. Also, gases that have a small effect on the radiative budget may still play an important role. For example, changing atmospheric concentrations of CO modify the oxidizing capacity of the atmosphere and consequently the level of atmospheric CH_4.

One way to examine the effects of these various feedbacks is to look at past records of climatic changes and atmospheric gases. Of the available atmospheric records, the most direct is obtained from ice cores. It integrates the complexity of all the system involved (terrestrial ecosystems, ocean, chemistry of the atmosphere, and climate), and reveals the net global response of the atmosphere to a given climate change. In this article, we review the reliability of the ice core record of critical greenhouse trace gases and describe and discuss its major features during different time periods.

The currently available ice record of-greenhouse gases comes from shallow and deep cores (Table 1) drilled both in Greenland and Antarctica (Fig. 1). This record is documented in detail for the recent period (the last ~ 200 years) and extends with less

The Ice Record of Greenhouse Gases

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Gases trapped in polar ice provide our most direct record of the changes in greenhouse gas levels during the past 150,000 years. The best documented trace-gas records are for CO_2 and CH_4. The measurements corresponding to the industrial period document the recent changes in growth rate. The variability observed over the last 1000 years constrains the possible feedbacks of a climate change on the trace gases under similar conditions as exist today. Changes in the levels of greenhouse gases during the glacial-interglacial cycle overall paralleled, at least at high southern latitudes, changes in temperature; this relation suggests that greenhouse gases play an important role as an amplifier of the initial orbital forcing of Earth's climate and also helps to assess the feedbacks on the biogeochemical cycles in a climate system in which the components are changing at different rates.

Man has caused large increases in atmospheric concentrations of CO_2, CH_4, and N_2O since ~ 1800, and of chlorofluorocarbons (CFCs) since 1950. We urgently need to understand how sensitive Earth's climate is to the radiatively active gases (also called greenhouse gases). We also need to understand how changing climate affect the biogeochemical cycles of these gases.

After an initial temperature change induced by a modification in greenhouse gases, several important feedbacks determine the climate sensitivity. They include (i) changes in the atmospheric content of water vapor (which is another greenhouse gas), (ii)

changes in the surface albedo resulting from modifications in snow and ice cover and to a lesser extent in vegetation, and (iii) changes in cloud distribution and content. Most of these parameters are included in the general circulation models. The results of most simulations of a doubling of atmospheric CO_2

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Table 1. Main characteristics of the ice cores from which greenhouse gases have been measured. Camp Century and Dye 3 are from Greenland, the other cores are from Antarctica.

Ice core	Depth (m)	Year	Elevation (m)	Mean temperature (°C)	Mean accumulation (g cm^{-2} yr^{-1})
Camp Century	1387	1966	1885	−24	32
Dye 3	2037	1981	2480	−19.6	50
Byrd	2163	1968	1530	−28	16
Dome C	905	1978	3240	−53	3.4
Vostok	2083	1982	3490	−55.5	2.3
DE08	234	1987	1300	−19	116
Siple	200	1983	1055	−24	50
D57	200	1981	2030	−32	45