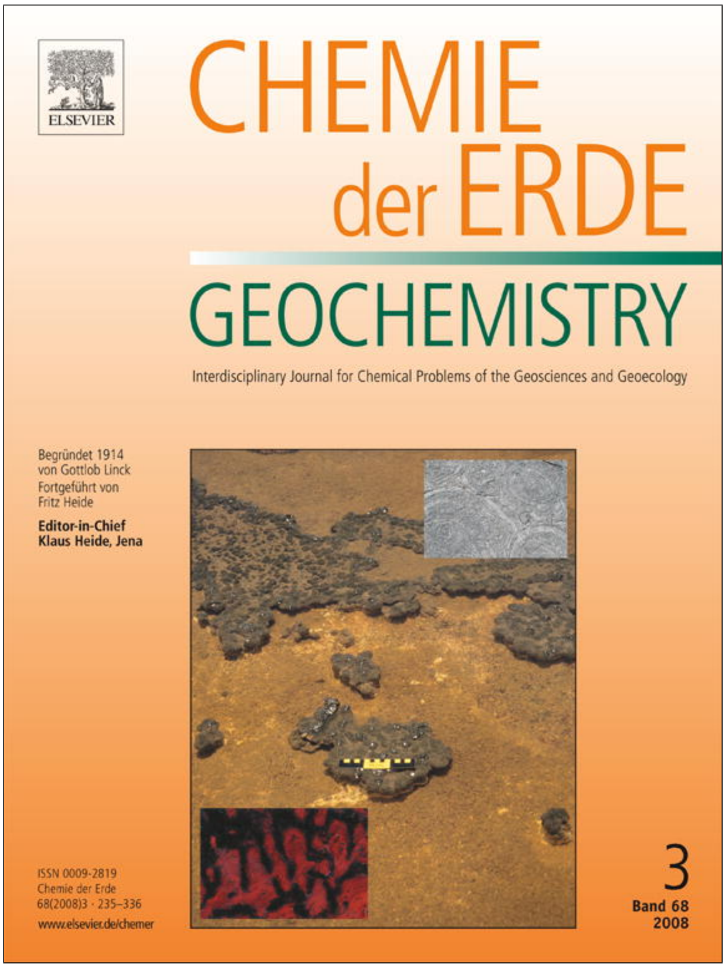
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INVITED REVIEW

Earth's atmosphere – Hadean to early Proterozoic

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Abstract

The chemistry of Earth's atmosphere during its first 2–2.5 Ga bears on several branches of geoscience including the origin of prebiotic molecules and life itself, early surface processes, the "faint young sun" problem, carbon isotope systematics, and the transition to an oxidized surface. The geologic record, as sparse as it is for this era, presents several difficulties for attempts to model the atmosphere and its changes through time. The prevailing view for the past 50 years has centered around a moderately oxidized atmosphere of CO_2 and N_2, and most modeling efforts have been directed at reconciling geologic data, and atmospheric and chemical constraints, with such a composition. Improvements in modeling of early Earth processes and increased knowledge of Archean geology, including new geochemical methods and data, have largely helped support this view of the early atmosphere over the last 25 years, but have also left several nagging questions unanswered. How was a sufficient reservoir (and concentration) of prebiotic molecules produced? What were the major reservoirs for carbon, and how did they develop their isotopic signatures? Is there a solution to the problem of the "faint young sun"? Why was surface oxidation delayed following the advent of oxygenic photosynthesis? Lately, some attempts at answering these questions have suggested the importance of more reducing capacity at the early Earth's surface, but without abandoning the idea of a mainly CO_2–N_2 atmosphere. It may be that returning to ideas of the early atmosphere current during the 1940s and earliest 1950s could help resolve some of these problems. Such an approach may not only be consistent with the atmospheres of the other terrestrial planets, but may help answer significant questions about the surface history of Mars.

Keywords: Early atmosphere; Earth; Volatiles; Faint young sun; Mars

1. Introduction

The origin and evolution of Earth's atmosphere are subjects intimately intertwined and very broad in scope. Questions of the source of the necessary volatiles, original atmospheric composition, nature and timing of compositional changes, and effects of atmospheric properties on global conditions and processes have entertained geoscientists and atmospheric scientists for decades. Any attempt to comprehensively review this work is almost certain to be either overwhelmingly lengthy or to fall short of completeness. Fortunately, there have been several reviews of various important aspects of the full picture at various times in the past, including discussions of the general problem (Walker, 1977; Holland, 1984), aspects of isotopic and rare gas compositions (Pepin, 1991, 2006), considerations of oxidation state (Blankenship, 1992; Canfield, 2005; Catling and Claire, 2005) and accretion and sources of volatiles (Mottl et al., 2007; Righter, 2007). The collections of papers in Atreya et al. (1989), Canup and Righter (2000) and in *Elements*, Volume 2:4 (2006) cover many of the topics of interest in individual articles.

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No attempt will be made here to repeat the comprehensive treatment of Holland (1984), or to be as comprehensive in treating the more recent work. Greater detail as to specific aspects covered somewhat superficially in this review, and more extensive lists of references, can be found in the more recent reviews mentioned above.

This review addresses developments of the last 20–25 years, covering as much of the breadth of the issues as possible, but focusing on those aspects that shed light on a few major problems yet to be resolved. Considerable work and thought during the past 20 years has shed light in several interesting areas, but without as yet leading to a consensus view on several. Some of the topics covered in this review help define ranges of possibilities, either constraining or permissive. Extant problems are often only made apparent by considering lines of evidence from seemingly disparate fields. The main goal of this review is to make connections that clarify the essence of unresolved issues and major topics, ordered approximately by time.

It should be noted that the atmosphere cannot be considered in isolation from the hydrosphere (or even the lithosphere). For convenience "atmosphere" should be construed throughout (unless otherwise specified) as including the oceans, principally because the exchange of materials between the two takes place on time scales short compared to geologic time. Exchanges between (mostly) oceans and lithosphere are significant, but usually take place on time scales close to geologic. These are important in several ways that will be apparent from the discussion.

2. A brief historical review

One of the early discussions of the general problem of the origin of Earth's atmosphere (Landsberg, 1953) appeared just as modern ideas about the atmosphere were emerging from geologic data and observations of geologic processes (Rubey, 1951, 1955). Prior to this time there were few constraints on the possibilities for ancient atmospheric composition, and even fewer on its evolutionary history. Landsberg (1953), following the prevailing view at that time, described the earliest atmosphere as being highly reducing, consisting of various hydrogen-containing compounds (although, oddly, not methane). He also considered this atmosphere to have been highly ephemeral, and rapidly replaced by a subsequently degassed (from the interior) atmosphere dominated by carbon dioxide and nitrogen. This latter was consistent with the view of Rubey (1951) that volcanic gases were the main source of the atmosphere and oceans. The conditions necessary for synthesizing prebiotic molecules (Oparin, 1938; Haldane, 1954; Miller, 1953) also supported a highly reducing initial atmosphere, of uncertain duration. Rubey's (1951, 1955) analysis was the firm foundation for positing an atmosphere of nitrogen, water vapor and carbon dioxide throughout the Archean, a view that has since dominated thinking about this phase of atmospheric history.

Holland's (1984) review and analysis can be taken as the prevailing view as of that time, a view that has largely been supported by subsequent work. His detailed approach using thermochemical treatments and broad geological inputs defined many of the constraints and ranges of possibilities for the Archean atmosphere. He also clearly described several unresolved issues. The following summary covers those aspects of importance to the present review.

(1) Earth's volatile inventory was originally incorporated in condensed phases in the cooling solar nebula. The volatile inventory of Earth can be largely explained by degassing of a small proportion of the total amount of meteoritic solids accreted to form the planet. The importance of directly accreted volatiles is probably minimal, and homogeneous accretion of Earth was probably dominant. The Earth is strongly depleted in a wide range of volatiles compared to solar abundances, including both light and heavy rare gases.

(2) Early degassing may have involved volcanic gases produced by equilibration of magmas in contact with metallic Fe–Ni, but these were probably soon replaced (following sinking of Fe–Ni into the core) by more oxidized gases. Early production of substantial H_2 and CO was followed by mostly H_2O and CO_2.

(3) Primordial gases are still being released from the mantle, but 50% or more of the volatiles were likely degassed during the first 1–200 million years of Earth's history. A magma ocean may have been an important factor in developing the early atmosphere, especially in terms of the distribution of magma-soluble volatiles such as water.

(4) If high levels of H_2 (and CO) were produced, photochemical and atmospheric processes would have led to the production of reduced carbon compounds, perhaps initially CH_4. The photochemical instability of CH_4, however, would quickly lead to production of more condensable carbon compounds which would end up in the oceans. Reactions between sea water containing organic compounds and volcanic rocks at a few hundred degrees would produce CH_4 (and NH_3), but not in quantities sufficient to maintain the reducing atmosphere envisioned by Miller (1953), given the sensitivity of both gases to photochemical destruction. "The organic chemistry of the early oceans was probably extraordinarily complex" (Holland, 1984).

(5) Carbon dioxide soon became the dominant carbon species in the atmosphere, but its concentration

during Archean time is unknown and was possibly quite variable. Weathering reactions involving carbonation and hydration have been going on from earliest times. The enhanced greenhouse effect necessary to counteract the faint young sun may have been due to substantially higher levels of CO_2 in the Archean atmosphere. Although there is very limited evidence to indicate precise levels of atmospheric CO_2 throughout much of the Archean, analysis of weathering near the end of the Archean suggests that CO_2 levels by that time were lower than required to maintain moderate surface temperatures.

(6) Several lines of evidence suggest very low levels of atmospheric oxygen throughout much of the Archean, and low levels of free oxygen by the end of the Archean, but the precise levels are difficult to determine. Oxygen levels remained low during the early Proterozoic. Evidence of oxygenic photosynthesis during the early to mid Archean was minimal, but it probably began by 2.7 Ga and became a significant source of oxygen by the early Proterozoic. A late Archean rise in atmospheric O_2 was likely due to oxygenic photosynthesis. The continued very low level of oxygen following the advent of oxygenic photosynthesis may have been due to nutrient limitations on biologic productivity, in particular phosphorus availability.

These aspects of Earth's early atmosphere are generally accepted at present, although there are a few dissenting voices. Many of these conclusions continue to be tentative, and there are several areas where the available evidence allows, if not encourages, a broader range of interpretations. Since Holland (1984) there have been several discoveries, measurements and modeling efforts that cast light on these remaining problems, but it is fair to say that several matters have defied the best efforts at resolution. Still, our picture of Earth's early atmosphere has improved, and a review of the current situation is warranted.

Anyone working in this area will probably adopt Walker's (1977) attitude toward questions and answers regarding Earth's early atmosphere: "Where clear evidence is lacking, it has been necessary to guess what might have happened. Much of this account of atmospheric evolution is therefore speculative. Many of my guesses may be wrong, but if my version of atmospheric history stimulates the development of more accurate histories I shall be well pleased." Holland (1984), in a similar vein, discussing the earliest atmosphere: "All that can be done at present is to reconstruct the state of the early Earth as imaginatively as possible, to set reasonable limits on the range of the parameters that seem to be important, to treat this current vision of the early Earth with as much rigor as our present understanding permits, and to remain skeptical of the results". I certainly endorse these views in writing this review.

3. The source of the volatiles: meteorites and planetesimals

The consistency between meteorite, terrestrial planet and solar compositions of refractory elements is one of the most persuasive arguments for the common origin of these objects. This also argues for the origin of Earth's volatiles from the same (or at least a similar) source (Holland, 1984). Drake and Righter (2002) and Burbine and O'Brien (2004) reviewed the question of the specific source of earth-forming materials (including the source of volatiles) and concluded that extant meteorites (or at least chondrites) do not include samples/mixes that match terrestrial compositions, either in terms of elemental abundances or isotopic signatures. Their analysis, however, does not preclude other mixtures of meteoritic (and cometary) materials as sources of either the solid Earth (indeed, they specifically allow that terrestrial oxygen isotope ratios could be produced by a meteorite mix) or the volatiles. Mottl et al. (2007) provide a very detailed review of volatiles in the early Solar System, with special emphasis on the source(s) of planetary water, underlining the uncertainty as to specifics of source(s). Considering the complex processes that would accompany just the latest stages of accretion, it is questionable whether any simple comparison of meteorite types with primitive upper mantle compositions (including considerations of the "late veneer") should be expected to produce a close match with particular meteorites or meteorite classes. Earth's upper mantle and Earth's volatile reservoirs surely express the results of mixing of a wide array of late-arriving objects with the pre-existing accreted material, and complex processing involving impact, magmatic, hydrothermal and atmospheric chemistry. It seems unlikely that any simple model comparisons would be definitive. Aspects of some of these accretional processes relevant to Earth's early atmosphere will be discussed in more detail in the next section. Even if volatile components of extant meteorites do not match the chemistry of Earth's atmosphere, the volatiles for that atmosphere must have come from some collection of volatile-bearing accreted materials, whether early or late arriving.

The necessary loss of volatiles from the terrestrial planets and meteorites is obvious in terms of hydrogen and helium contents, but the depletion in heavier noble gases provides additional constraints on early nebular processes (Humayun and Cassen, 2000; Pepin, 1991). Yet another constraint is imposed by the condensable volatiles, especially hydrogen compounds of oxygen, carbon and nitrogen (Sill and Wilkening, 1977). The exact composition and timing of assembly of the material accreting to form Earth (and the other terrestrial planets) is subject to speculation, giving rise to a range of accretional histories bounded by the extremes of inhomogeneous and homogeneous accretion.

An analysis of the current infall of meteoritic material can be enlightening. The Antarctic Meteorite Program has produced a sampling of meteorite falls (Table 1) (Grossman, 1994) that may be representative of accreting material, perhaps more true of the present era than of times in the distant past, but in any case this is one of the few measurables that are available. Table 2 is a summary of volatile compositions of several meteorite classes.

We can conclude two things from these tables, assuming that the collection is at least somewhat representative. First, the mass of irons in the falls is approximately 14% of the total, somewhat less than the metal fraction of Earth, but still substantial. The meteorite mix includes a range of materials from the most refractory to the most volatile-rich. This is a strong argument against inhomogeneous accretion (Holland, 1984). It is not unreasonable to assume that the current infall mix is a fair approximation to what we may refer to as the "late-accretional" mix, that is, the last 1–2% of the total mass accreted after the Moon-forming impact. It may even be representative of most or all of the earlier accretional history.

Second, if 1% or more of late-accreting material is carbonaceous chondrite (Table 1), and if it degasses during or after accretion, then the entire present atmospheric inventory *could* be accounted for by as little as 1% of Earth's total mass (approximately equivalent to the outer 50 km of the planet) accreting as late-stage additions. The amount could even be much less, because ordinary chondrites (and irons) also contain significant volatiles (Table 2).

Table 1. Antarctic meteorites (Grossman, 1994)

Type	Mass (g)	% by mass
Stony meteorites	2,306,214	85.1
Irons	370,779	13.7
Carbonaceous chondrites	32,537	1.2

Stony irons are not included separately, as they comprise only about 1% of the total mass. Achondrites and chondrites are lumped as stony meteorites. Carbonaceous chondrites are listed separately because of the importance of their volatile components.

Table 2. Volatiles in meteorites

Meteorite	H	C	N
C1 chondrites (Orgueil)	2.02	3.22	0.32
CM chondrites		0.35	
H chondrites	0.32	0.12	34 ppm
L chondrites	0.34	0.16	34 ppm
LL chondrites	0.6	0.235	50 ppm

In wt% except as indicated. (Palme and O'Neill, 2003; Bradley, 2004; Schaefer and Fegley, 2007).

Addition of volatiles by late accretion of cometary material is also a possibility (Morbidelli et al., 2000), but not necessity. Compositional and isotopic abundances favor carbonaceous chondrites relative to comets (Abe et al., 2000; Kramers, 2003). Drake and Righter (2002) limit cometary contributions to less than 50%, but Mottl et al. (2007) suggest caution as to the possible cometary component. Some contribution of volatiles by cometary accretion implies that even smaller amounts of late meteorite accretion are needed to produce the total volatile inventory.

Finally, note that most of the carbon in meteorites and comets is in the reduced state (Hayes, 1967), as organic compounds, and this may be significant to the oxidation state of the earliest atmosphere.

4. Accretion: timing, rates and processes

Whereas the nature of the solar nebula imposes some compositional constraints, they are pretty loose when one considers the possible variety of accretionary processes, histories and mechanisms (Righter, 2007; Mottl et al., 2007). On a number of issues there is little doubt. For one, Earth has lost a major fraction of the mass of the volatile elements present in the nebula (Brown, 1949; Prinn and Fegley, 1987; Pepin, 1991; Kramers, 2003). The gas giants are much better approximations to solar composition than are any of the terrestrial planets. Processes in the early nebula led to significant fractionations, based primarily on volatility of the elements/compounds present, and on reactions and/or condensations that took place during nebular evolution (Prinn and Fegley, 1987). Second, whereas several volatiles are depleted on Earth, some appear in significant amounts, making up the present atmosphere and hydrosphere. These remnant volatiles largely derive from low-temperature condensates ("ices"), e.g., water and various carbon and nitrogen compounds, or other solids such as hydrates, hydrous minerals and high-molecular-weight carbonaceous compounds (Prinn and Fegley, 1987). On the other hand, the non-radiogenic noble gases, even those with high atomic weights, are strongly depleted on Earth. This is powerful evidence for a "cold" era of accretion, in which gravitationally incompetent (small) particles carrying condensable/high molecular weight volatile-rich phases collect on growing planetary-scale objects where the volatiles (following degassing) are trapped by the larger gravity field, while the inert volatiles are dissipated from the collection of small bodies into the outer reaches of the nebula *before* the large bodies accrete in the inner solar system.

Accretion is inaccessible to direct study, so our insights into the process are limited to inferences from observations of the results, and to various models that (we hope) mimic the process of accretion. This has been an active field with varied, and sometimes convergent, results (Hanks and Anderson, 1969; Turekian and Clark, 1969; Safronov and Koslovskaya, 1977; Safronov, 1978; Grossman and Larimer, 1974; Wetherill, 1976; Weidenschilling and Cuzzi, 1993; Wetherill and Stewart, 1993; Chambers, 2004; Raymond et al., 2004; O'Brien et al., 2006; Köberl, 2006b, and several papers in Canup and Righter, 2000). An important adjunct to "simple" accretion models is the "large impact" hypothesis for formation of the Moon (Hartmann and Davis, 1975; Cameron and Benz, 1991; Cameron, 2000; Canup, 2004), an event that must have occurred after a significant amount of material had accreted to form both Earth and the impacting (Mars-sized) object. This event occurred about 50 My after the beginning of accretion (Nisbet and Sleep, 2001; Halliday, 2004). This constraint is consistent with core formation on Earth at around the same time or slightly earlier, as evidenced by Hf/W and Nd isotope systematics (Halliday et al., 2000; Yin et al., 2002; Kleine et al., 2002; Schönberg et al., 2002; Boyet and Carlson, 2005). There are two points here that are important to considerations of Earth's atmosphere.

First, accretion occurred fast enough, especially with the peak energy release associated with the Moon-forming impact, to result in an internally hot early Earth (Safronov and Koslovskaya, 1977; Safronov, 1978; Nisbet and Sleep, 2001; Righter, 2007). The energy released in core formation added its contribution to impact heating. Late (perhaps 3.9 Ga) impacts of large objects could have produced significant "local" surface melting (Grieve et al., 2006). This set the stage for degassing of volatiles from the accreted material by heating, and particularly points to early substantial degassing. Second, assuming a significant amount of degassing preceded the giant impact, that event would result in major loss of volatiles from the planet (Nisbet and Sleep, 2001), as evidenced by rare gas compositions (Porcelli and Pepin, 2000). This volatile loss is essential to prevent the formation of a truly massive atmosphere from the cold-accreted planetesimals. In fact, Earth is volatile-depleted compared to probable meteorite mixes that seem likely as seed material for planet formation (Kramers, 2003), in addition to being depleted relative to solar abundances. Other volatile loss processes have been suggested, such as atmospheric erosion by a T Tauri wind (Walker, 1977), although recent studies suggest that the T Tauri phase may be limited to the first several million years of solar system history, before most planetary accretion (Briceno et al., 2001).

It is likely that following the Moon-forming impact there was a magma ocean of considerable depth, both on Earth and Moon. The interaction of such a magma ocean with a residual atmosphere has been discussed (Nisbet and Sleep, 2001), but it seems likely that most of the volatiles now on Earth arrived subsequent to this time. One exception might be water dissolved in the magma ocean. If most volatiles did not arrive late we are left with the problem of how NOT to get a massive atmosphere.

Inhomogeneous accretion is generally rejected at present, though it cannot be completely ruled out (Drake and Righter, 2002). Among the reasons for its rejection is the need for significant equilibration between metal and silicate *after* a substantial amount of accretion takes place in order to produce the Hf/W and Nd systematics (Halliday et al., 2000; Yin et al., 2002; Kleine et al., 2002; Schönberg et al., 2002; Boyet and Carlson, 2005) that date core formation to at least 30 My after the beginning of accretion. In other words, the metal core cannot form first and remain separate from the silicate. If inhomogeneous accretion is rejected (in particular if late-accreting material resembles average Earth or "average meteorite" compositions), there is reason to doubt that late degassing of Earth's upper mantle took place in a metal-free environment, implying the possibility that reduced gases were produced (Holland, 1984), at least for the earliest atmosphere.

Just what fraction of Earth accreted late is highly speculative, but most models include an accretion tail (say post-90 My) of 1% or more of the total mass (e. g. Halliday et al., 2000; Walker et al., 2004; Chambers, 2004) (Figs. 1 and 2). One model that attempts to quantify late accretion rates concludes that about 10^{24} g might have been accreted between 4.15 and 3.8 Ga (Anbar et al., 2001). Their results were used to calculate the accretion of approximately 10^{22} g of reduced carbon compounds during that interval (Catling et al., 2001), about 15% of Earth's surface carbon inventory (including sedimentary rocks). Although Catling et al. (2001) used an improbably high carbon concentration in an average meteorite mix (1%), their result nevertheless suggests a significant fraction of the carbon inventory arrived late. A recent carbon history/cycling model assumes this late reduced carbon influx as an important condition (Hayes and Waldbauer, 2006). The amount of volatiles accreted between the Moon-forming impact (at about 4.5 Ga) and 4.15 Ga is speculative, but interpolation between the estimate of Anbar et al. (2001) and rates necessary to complete 90% of accretion at the end of the Moon-forming impact, could easily account for the complete volatile inventory as late-accreting material. Note that the so-called Late Heavy Bombardment (Turner, 1977; Hartmann et al., 2000; Köberl, 2004, 2006a, b), the apparent increase in impact rate evidenced by lunar cratering densities at around 3.9 Ga (Fig. 2), whether as a tail at the end of a continuous accretion or a "spike" in accretion rate,

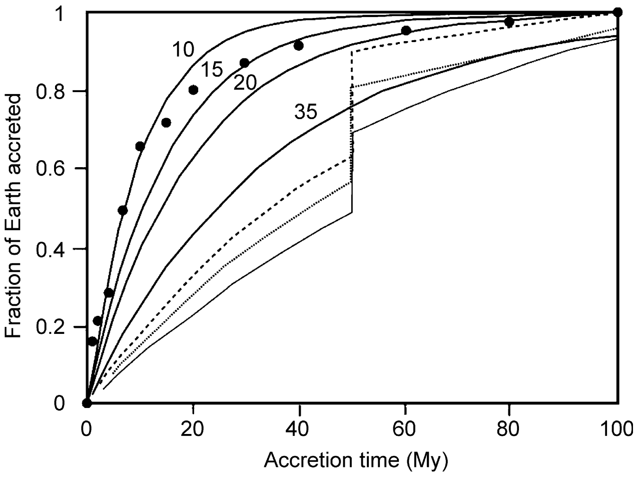

Fig. 1. Accretion models for Earth. Numbers next to curves are median accretion times in millions of years. Set of curves with "steps" at 50 million years are three cases including a Moon-forming impact at 50 My (after Halliday et al., 2000). Black dots are for averages of several models from Wetherill (1976). All but the most rapid of these models supports the idea that more than 1% of Earth's mass may have accreted after 50 My, or after a Moon-forming impact at that time.

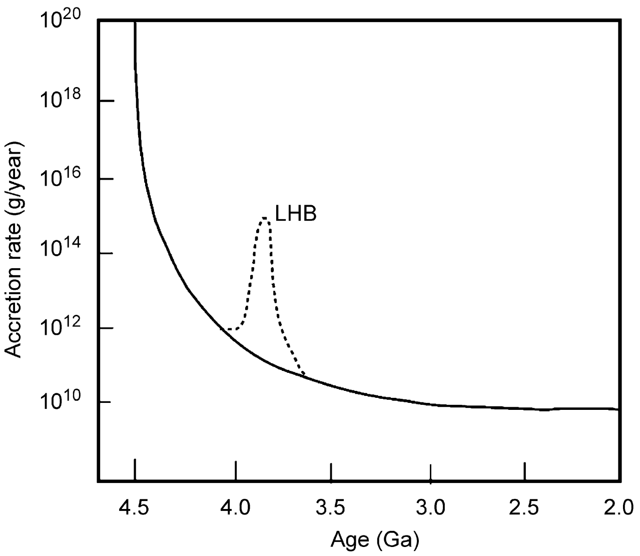

Fig. 2. Accretion rates for the Moon, including a "spike" for the Late Heavy Bombardment. Accretion rates for Earth would have been at least 20 times higher. The very high, though rapidly falling, accretion rates in the Early Hadean could easily account for accretion of more than 1% of Earth's total mass following the Moon-forming impact at about 4.5 Ga. After Köberl (2006a, b).

would probably amount to a small fraction of the total post-moon-forming impact accretion. Gomes et al. (2005) estimate the LHB of Earth amounted to about 2×10^{23} g, less than 0.01% of Earth's total mass, a number consistent with Anbar et al. (2001). Hartmann et al. (2000) previously gave an estimate of $0.8–30 \times 10^{23}$ g, in the same general range.

The history of accretion of Earth's volatile component is enormously complex, and unavoidably obscure (Mottl et al. (2007), but it is probably fair to say that, whatever the details, a significant amount of the late-accreting material that gave rise to the volatiles initially arrived as hydrous phases and reduced carbon compounds, accompanied by a significant fraction of metal.

5. Early degassing – early atmosphere

Earth's earliest atmosphere was the product of late-accretionary and internal heat-driven processes acting on late-accreting material mixed with the outer (fairly hot) parts of the Earth. Fifty percent or more of Earth's volatiles may have been degassed during this earliest phase of Earth history, probably before 4.2 Ga. Because the composition of the earliest atmosphere may be relevant to the origin of prebiotic molecules and to the subsequent evolution of the atmosphere, it is important to assess the range of possible compositions. Although Holland (1984) suggested a very short-lived phase with strongly reducing conditions resulting from degassing of H_2 and CO leading to formation of CH_4 (very briefly) and an unspecified quantity of organic compounds condensed onto/into the ocean, he also proposed that degassing quickly shifted to more oxidized gases (H_2O and CO_2) following core separation. He also suggested some minimal production of CH_4 through interaction of oceanic organics and silicates under hydrothermal conditions, but considered the effects of this on the atmosphere to be very minor. Because he did not specify the relative amounts of organic compounds and CO_2 production, the amount of reducing capacity stored as organic compounds from the earliest phase of the atmosphere remains an open question. Most discussions of atmospheric composition during the Archean invoke an atmosphere relatively rich in CO_2, with only minor amounts of reduced carbon species. This is a matter of some importance to the origin of life because of the difficulty of producing significant amounts of prebiotic molecules from such an atmosphere (Stribling and Miller, 1987; Kasting et al., 1993), at least without the addition of significant reducing capacity (Kasting et al., 1983; Zahnle, 1986; Kasting and Brown, 1998; Tian et al., 2005). It may be that the current state of knowledge allows for more reducing capacity at the Earth's surface than has been assumed since an early CO_2-rich atmosphere became the accepted model.

Early degassing processes include (at least): impact degassing (e.g., Lange and Ahrens, 1982; Ahrens et al., 1989), volcanic degassing involving equilibration between volatiles and magmas at temperatures of 1000 K (e.g., Holland, 1984) and hydrothermal degassing involving equilibration or reaction of volatiles and various silicate phases at temperatures of hundreds of degrees (e.g., Schaefer and Fegley, 2007). The details attending each of these processes are critical to the nature of the gases produced. For example, the presence or absence of metallic Fe during magmatic equilibration affects the oxidation state of the volatiles (Holland, 1984).

Impact degassing is the first stage of release of the volatiles in accreting objects. Based on the partitioning of impact energy into impactor and target (and between mechanical, kinetic and thermal), most of Earth's volatiles were released from projectiles on impact, either by shock-induced devolatilization or projectile vaporization (Ahrens et al., 1989; Fiske et al., 1995; Tyburczy et al., 2001; Ellwood Madden et al., 2006). Ahrens et al. (1989) calculate that more than 99% of Earth's volatiles were released during accretion. This estimate is higher than most other models of early degassing. The disparity is due, in part, to the survivability of smaller impactors slowed by the atmosphere. They estimate that atmospheric deceleration may be important for impactors up to 100 m striking either oceans or the atmosphere. Whether such objects [and somewhat larger ones might be important for dense atmospheres produced by massive early volatile release (Abe and Matsui, 1986, 1988; Matsui and Abe, 1986a, b)] comprised a significant fraction of the accreting mass during the accretionary tail is debatable, but clearly the volatile inventory depends on some mix of projectiles, some fraction of which must have come to rest at the surface with their volatiles largely intact.

The late-accretionary Earth had a solid surface, because magma oceans (even for something as large as the moon-forming impact) cool very rapidly, solidifying almost instantly on a geologic time scale (Nisbet and Sleep, 2001; Sleep et al., 2001; Köberl, 2006a). Within a few million years of the moon-forming impact the surface temperature dropped enough to allow liquid (water) oceans (Nisbet and Sleep, 2001; Zahnle, 2006), with the solid Earth mostly covered by ocean. Although the moon-forming impact may have blown away a large part of the previously formed atmosphere, some residue (especially water dissolved in the magma ocean) might have remained. Note that the water in such a magma ocean would be rapidly stripped back into the surface environment once a frozen rock surface formed and temperatures dropped enough for water vapor to condense from the atmosphere (again, a few million years at most). This is because surface magmatism from the convecting magma ocean would release volatiles at low ambient pressure at the surface after the massive (water) atmosphere condensed to liquid. The mass of this early ocean is unknowable, but could easily have been equal to the current ocean, if not greater. The ocean was probably global, with few if any continents and little continental crust in the strict sense. Emergent parts of the silicate surface were confined to island-arc-like settings (Köberl, 2006a).

Continued bombardment of this (post-moon-forming-impact) surface can be envisioned in three basic forms:

(1) "small" projectiles up to perhaps hundreds of meters diameter that would simply add to the surface accumulation without immediately releasing volatiles on impact.
(2) Projectiles with dimensions up to perhaps 100 km, parts of which would deposit undegassed fragments on the surface but would largely inject volatiles (and vaporized solids) into the atmosphere. The fraction of each of these is uncertain, but probably favors the second as the impactor size increases.
(3) Large projectiles that might largely vaporize on impact, along with significant amounts of the target surface. Such impacts would also probably form large, short-lived melt pools (Grieve et al., 2006).

The relative masses of these groups are unknown. Evidence from lunar crater densities, or at least those related to the Late Heavy Bombardment (Zahnle and Sleep, 2006; Köberl, 2006a, b), and modeling of accretion (e.g., Wetherill, 1976) suggest Group 3 may be the largest. Modern meteorite falls demonstrate some fraction is in Group 1. Accreted material in the first group and any undegassed material in the second group simply adds a primitive layer at Earth's surface. This layer will eventually be processed by endogenous thermal sources of two kinds: volcano-magmatic and hydrothermal.

Virtually all previous discussions of magmatic degassing argue for production of oxidized gases by equilibration of carbon phases with molten silicate in the absence of iron, once core separation has occurred (e.g., Holland, 1984). Because core formation preceded the moon-forming impact, and thus the late-accretionary tail (the likely source of the extant volatile inventory), one might assume that degassing of the late-accreting material by volcano-magmatic activity would directly lead to a CO_2-rich atmosphere. However, if the (initially undegassed) accreting surface material resembles a modern meteorite mix, not only does it contain its own iron, but the major carbonaceous phases are mostly reduced compounds. In order to get the volatile fraction of these "fertile" materials into an environment where it can equilibrate with magma, it must be subducted. That is conceivable, but then the volatile-rich fraction would arrive in the magmagenic zone (probably in a subduction-like setting) *along with the metal-rich component*. In other words, the late-accreting material brings its own "core fraction" with it. This simply means that the initial degassing of surface-accreted meteoritic material by volcanic processing will necessarily involve production of reduced species even though the main phase of core formation has long since passed. Following Holland (1984), this means that the initial magmatic degassing of the "permanent" volatile inventory will result in production of a reducing atmosphere. Through photochemical and electric discharge processes this reducing (hydrogen-rich ?) atmosphere yields a large pool of reduced carbon compounds, either with methane as a short-lived intermediate species, or directly from reactions of H_2, CO, and other gases as per Tian et al. (2005).

Some (perhaps most) of the fertile accreted material will be processed at submagmatic temperatures. The thermochemistry of this possibility has been examined in detail by Schaefer and Fegley (2007) for ordinary chondrites at crustal pressures. Saxena and Fei (1988) performed similar calculations, including for carbonaceous chondrite compositions, at higher pressures. Schaefer and Fegley (2007) focused on ordinary chondrite parent bodies, but also applied their results to the early Earth. Briefly, their results and those of Saxena and Fei (1988) (and an unpublished Master's Thesis by Bukvic, 1979) point to production mostly of methane (and for temperatures of up to ca. 600 K, ammonia), at temperatures below the liquidus, i.e., up to about 1273 K. The effect on these calculations of including free iron in a representative meteorite mix is unknown, but is unlikely to result in more highly oxidized gases. Whatever the amount of pristine accreted material or likely conditions of degassing, both volcano-magmatic and hydrothermal processing would initially produce highly reduced gases and organic reaction products.

Group 3 material leads to a different scenario. To the extent that some part of each impactor survived without complete vaporization, some degassing would resemble that from the strictly small-impactor model, that is, reduced gases would be produced. If, on the other hand, we assume that the impactor completely vaporized and degassed its entire volatile inventory (Ahrens et al., 1989), the atmosphere received a sudden injection of new volatiles (while maybe losing some amount to impact erosion). It also experienced a sudden temperature rise and dust and silicate/metal vapor injection (Zahnle, 2006). The hot atmosphere boiled some part of the ocean, but for impactors of the expected sizes did not completely vaporize whatever ocean was present (Nisbet and Sleep, 2001; Zahnle, 2006). Atmospheric temperature then dropped rapidly to levels sustainable by whatever greenhouse effect existed (Abe and Matsui, 1988). The extreme example of the moon-forming impact results in very high atmospheric temperatures dropping to about 500 K in about 2500 years (Zahnle, 2006). Events in the accretionary tail were probably less energetic by at least one, and probably two, orders of magnitude. The high-temperature (>500 K) phase for these smaller events must have lasted no more than a few hundred years at most. Previous discussions of the nature of the gases in this impact-generated atmosphere argue for CO_2 as the dominant carbon species (Nisbet and Sleep, 2001; Zahnle, 2006) based on the high temperatures involved and presumed loss of reducing capacity (hydrogen) to space. However, the short lifetime of the high-temperature state of the atmosphere and the presence of enormous reducing capacity suggest a different conclusion. Complete vaporization of a 6×10^{24} gm impactor (about 1% of the mass of the moon-former) of average meteorite composition would put about 2×10^{24} g of iron vapor into the atmosphere. The vaporization of water in the impactor and from any extant ocean would add large amounts of water as well. Reaction of water and iron vapor in the high-temperature atmosphere would generate as much as 4×10^{22} moles of hydrogen, nearly 1 atmosphere equivalent. Even if rapid condensation of the iron led to rainout, reaction between this iron and water would rapidly produce hydrogen. Whatever the form of the vaporized carbon compounds (which contribute additional hydrogen) originally in the impactor, they would be "bathed" in a hydrogen-rich atmosphere. At peak temperatures the equilibrium carbon phases may well have been oxidized, although this depends on details of total atmosphere mass (pressure) and relative amounts of the various species. Within a few hundred years, cooling of the atmosphere to <500 K clearly makes methane the stable carbon species if hydrogen concentrations remain high (see Fig. 2.3 of Delsemme, 1997). [A lesser degree of reduction has been envisioned by a similar mechanism for the production of CO from impacts of ordinary and carbonaceous chondrites onto an Earth with an initially CO_2-rich atmosphere (Kasting, 1990, 1993).] Does the hydrogen stay in the atmosphere long enough?

The modern rate of hydrogen escape from Earth is about 4×10^{10} moles/yr (Catling et al., 2001). It has been estimated that loss of hydrogen in the late Archean may have been 2–3 orders of magnitude higher due to higher methane abundances (Kasting, 2005; Kasting et al., 2001; Catling et al., 2001; Kharecha et al., 2005), and it presumably would have been even higher with a massive hydrogen-rich atmosphere. However, even if the post-impact hydrogen escape rate was five or six orders of magnitude higher than at present, and the vaporization of the metallic fraction of the impactor was as little as 1% of the total metal, the atmosphere would have retained very high levels of hydrogen after atmospheric temperature dropped well into the methane stable range a couple hundred years after the impact. Note that this argument does not depend on the size of the impactor, so long as it is large enough to lead to substantial vaporization. Although smaller impactors produce proportionately smaller amounts of iron vapor/hydrogen, they also produce proportionately less heating of the atmosphere, and thus shorter lifetimes for the high-temperature phase of the atmosphere. If impactor sizes are small enough, we revert to the situation where substantial amounts are not vaporized, i.e., endogenic degassing occurs from a reduced (iron-rich) solid surface layer.

Subsequent conditions of the post-impact atmosphere/surface depended on atmospheric composition and how it changed with time. It is possible that greenhouse gases helped maintain temperatures of a few hundred degrees or so as a consequence of a substantial greenhouse effect (Abe and Matsui, 1988). Models proposed for a steam or steam/CO_2 atmosphere following the moon-forming impact (a much larger event) suggest such conditions may have lasted for thousands of years (Nisbet and Sleep, 2001; Zahnle, 2006), and clearly for much less time for smaller late impacts. The atmosphere would not have experienced temperatures above several hundred degrees for more than a hundred years or so, and would be highly reducing during and after that time. This is a vital constraint in considering the chemistry of the atmosphere and oceans during this initial interval. As it cools, the hydrogen-rich atmosphere resulting from a large impact either produces methane directly or leads to photochemical production of condensable carbon compounds (Tian et al., 2005). The stability of heavier carbon compounds depends on the prevailing surface temperatures, which may remain elevated for some time due to greenhouse conditions. Eventually production of these complex species, either directly or from photochemical destruction of methane, leads to significant rainout of heavier carbon compounds into the ocean. Continued chemical processing would produce a wide array of reduced carbon species, either dissolved in sea water or as an immiscible (probably floating) “goo”. Some of this carbonaceous material may settle to the sea floor, especially if attached to silicate debris.

Group 2 material, again an indeterminate fraction of the total accreting mass, must behave as some combination of the two scenarios above. While much of Group 2 degassed without vaporizing substantial iron, or without leaving undegassed material at the surface, the impact degassed carbon compounds would have been in a reduced state, and would have found themselves in a reducing atmosphere resulting from the other two groups of accreting matter.

Because these processes occur throughout the time of the accretionary tail, and include the prolonged period of subduction and subsequent degassing of primitive surface material, an early reduced atmosphere could be maintained for 100 million years, with a more or less continuous rainout of organics. This leads to highly favorable conditions for the generation of life, whether in near-surface or deeper environments, especially if dissolved carbon compound concentrations are as high as they could be, based on Earth’s present carbon inventory. One percent or more organic carbon in solution is possible.

Finally, the early atmosphere may well have acquired a significant amount of carbon dioxide. The major source would have been volcanism. This is not in contradiction to the above discussion of degassing of primitive material. Not all subducted material would contain the primitive meteorite mix, and the fraction of primitive iron-bearing material subducted would have decreased throughout the late-accretionary period (over 100 million years or so). The solid surface was largely the product of basaltic (komatiitic) magmatism, from which the free metal had been removed during magma genesis. Subduction and remelting of this metal-free crust would give rise to CO_2 from carbonaceous material it contained.

The composition of the early atmosphere was the result of several dynamic processes, some of which probably produced reduced carbon species while others produced CO_2. The composition may even have alternated between more reduced and more oxidized through time as different processes or events temporarily dominated. Eventually, as accretion waned, production of volcanic CO_2 became more important. Whereas 55 years ago an early methane-ammonia atmosphere was preferred, and for the past 50 years a carbon-dioxide-rich atmosphere has been the standard model, it appears that the situation may be more complex, with processes acting to produce both oxidized and reduced carbon species over an extended period of late accretion.

6. Climate: the faint young sun problem

One of the most vexing problems in the early history of Earth’s atmosphere and climate is the “faint young sun” paradox (Newman and Rood, 1977; Gough, 1981; Sagan and Chyba, 1997; Guedel, 2007). The essence of the problem is the difficulty of producing a moderate climate (presence of liquid water) at a time when the luminosity of the sun was 20–30% less than at present. The evidence for liquid water is strong for the early Archean, and only slightly less so for as early as 4.4 Ga (Wilde et al., 2001; Peck et al., 2001; Mojzsis et al., 2001; Valley et al., 2002; Nutman, 2006). Suggestions that the necessary warm climate was due to a more massive early sun (Sackman and Boothroyd, 2003) have been countered by observations of limited mass loss from the sun and comparable stars (Wood et al., 2005; Minton and Malhotra, 2007). The only solution is an atmosphere with high enough concentrations of greenhouse gases to counteract the lower solar luminosity. As is well known, methane and carbon dioxide are likely candidates, water being a condensable phase that adds a significant effect only if the basic warm climate can be provided by the more volatile phases. Holland (1984) addressed this problem and the proposed solutions at that time, concluding that “the problem seems to be unresolved at present; its solution may involve a better understanding of the paleogeography of the Earth…or of the greenhouse effect produced by atmospheric CO_2, or the demonstration that gases other than CO_2 contributed significantly to the greenhouse effect on the early Earth." This problem has received significant attention in the last 20 years, and its solution has important implications for the nature of the early atmosphere.

Carbon dioxide has been considered the most likely candidate for the early greenhouse gas based on models of production of Earth's secondary atmosphere, either by degassing of the mantle (Rubey, 1951, 1955) or impact release of gases during the late stages of planetary accretion (Ahrens et al., 1989). If conditions favored production of oxidized carbon species, especially CO_2, it is straightforward to imagine a CO_2-driven greenhouse effect sufficient to counteract the faint sun (Walker et al., 1981; Kasting and Brown, 1998; Ohmoto et al., 2004; Lowe and Tice, 2004; Hessler et al., 2004; Kasting and Ono, 2006). On the other hand, CO_2 reacts with silicates to produce strong weathering effects and deposition of carbonate minerals. The evidence for and against high concentrations of CO_2 in at least the late Archean and early Proterozoic atmosphere, based on considerations of weathering products, has been the subject of considerable recent discussion (Ohmoto et al., 2004; Kasting, 2004; Sleep, 2004; Ohmoto and Watanabe, 2004; Lowe and Tice, 2004; Hessler et al., 2004). Stripping of CO_2 from the atmosphere (Sleep and Zahnle, 2001; Zahnle and Sleep, 2002) over a geologically short interval could lead to planetary cooling, or even a frozen surface, quite the opposite of what is needed. The effectiveness of CO_2 removal depends on the availability of a reservoir to store the chemically bound carbon dioxide.

It would require about 0.2 atmosphere equivalent of carbon dioxide to overcome the faint young sun during the earliest times (Kasting, 1993), and only slightly less with the increasing luminosity of the sun as much as 1–2 billion years later. This concentration is thought to be unsustainable for geologic intervals, given the reactivity of CO_2 with silicates (Zahnle and Sleep, 2002). On the other hand, recycling of CO_2 back into the atmosphere, either at subduction zones or ocean ridges, could theoretically maintain high atmospheric levels, but this would imply continued high silicate weathering and carbonate mineral deposition throughout the Hadean and Archean. The problems associated with high early atmospheric CO_2 have been explicit for some time (Rubey, 1951, 1955) and continue to conflict with invoking CO_2 as the agent to overcome the climate paradox, as noted by Holland (1984) and Kasting (2005). One possible solution is to simply accept that Earth experienced a period of ice-house conditions during much of the Hadean, assuming the early-released CO_2 was reabsorbed into the lithosphere (Zahnle, 2006). Evidence for the presence of liquid water could be explained by local hydrothermal environments or occasional impact-generated warm intervals.

Methane originally received attention as a possible early greenhouse gas (Sagan and Mullen, 1972; Kiehl and Dickinson, 1987; Kasting, 1997; Pavlov et al., 2000), but was generally rejected because of its short lifetime in an atmosphere subject to ultraviolet radiation (Kasting et al., 1983; Levine, 1985; Zahnle, 1986; Kasting and Brown, 1998). Questions concerning lifetimes and rainout of a photochemically produced organic haze further complicate the picture. The presence of such an organic haze and methane-rich atmosphere on Titan are intriguing, but have mostly stimulated speculation on how methane is generated on Titan (Loveday et al., 2001; Atreya, 2007).

The recent revival of interest in methane as a greenhouse gas during the late Archean and early Proterozoic (Pavlov et al., 2001; Kasting et al., 2001; Kasting, 2005; Kasting and Ono, 2006) appears to be driven by correlations between the rise of atmospheric oxygen, carbon isotope anomalies and climate cooling at around 2–2.3 Ga (Pavlov et al., 2000, 2001; Kasting et al., 2001; Kasting, 2005; Haqq-Misra et al., 2007). In the late Archean, however, there is a reasonable source for regenerating methane. Methanogenic organisms are of very ancient lineage (Woese and Fox, 1977), were certainly present in the late Archean, and can generate significant methane from reduced carbon or other sources of reduction capacity, e.g., hydrogen. Although some methane production may be due to inorganic mechanisms such as serpentinization of oceanic ultramafic rocks (Kasting and Brown, 1998; Kelley et al., 2005), organic sources are generally favored as more potent. It may be that biologic methanogenesis was also important in the early Archean, and even the Hadean, but direct evidence for methanogens at such early times is minimal.

There is, however, an inorganic mechanism for methane production with the potential to produce sufficient quantities to offset photochemical destruction and thus maintain an early warm climate, even on a prebiotic Earth. Theoretical calculations (Seewald et al., 1990, 1994), field observations (Seewald et al., 1994; Cruse and Seewald, 2006), and laboratory experiments (Seewald et al., 1990, 1994, 2006; Seewald, 2001) demonstrate that hydrothermal systems can produce large amounts of methane (and ammonia) if in contact with reduced carbon compounds. Modern hydrothermal systems are known to produce methane (and other hydrocarbons), some of which may be from serpentinization (Von Damm et al., 1985; Kelley et al., 2001, 2005; Proskurowski et al., 2008), although a role for methanogens cannot be ruled out in all cases. Hydrothermal experiments on carbonaceous sediments clearly demonstrate that biological processes are not essential, and that serpentization is not necessary if organic compounds are present (Seewald et al., 1990, 1994, 2006; Seewald, 2001). The main question is whether this mechanism can provide a high enough rate of methane generation, and for a long enough time, to produce a mild climate throughout the Hadean and Archean. This question arises because a loss of reducing power necessarily accompanies hydrogen escape to space (Catling et al., 2001), a process that continues right up to the present. Photochemical destruction of methane would have been a major source of atmospheric hydrogen in a methane-containing reduced atmosphere. Current H_2 loss rates are not sufficient to oxidize the surface, even over billions of years, but escape rates may have been significantly higher in the past, especially if the atmosphere contained enough methane to provide the requisite greenhouse warming (Catling et al., 2001; Pavlov et al., 2001; Kasting, 2005; Kharecha et al., 2005).

Kasting's (2005) calculations showed that as little as 100 ppm CH_4 in an atmosphere with 370 ppm CO_2 can maintain surface temperatures above freezing at 2.8 Ga with a solar luminosity 20% less than the present. Carbon dioxide levels of this magnitude, which are not in conflict with geological data, are postulated to avoid the formation of the organic haze that would produce an antigreenhouse effect. On the other hand, a recent re-examination of this model (Haqq-Misra et al., 2007) pointed out an error in the previous work of Pavlov et al. (2000) that invalidates their conclusion that low levels of methane would provide a sufficient greenhouse warming. Presumably, this new result also invalidates the quantification proposed in Kasting (2005), which depends on calculations made by Pavlov et al. (2001) similar to those of Pavlov et al. (2000). Haqq-Misra et al. (2007) do allow for sufficient greenhouse warming if CO_2 concentrations of 0.03–0.05 bar are accompanied by CH_4 concentrations of 1000 ppm, by including the effects of ethane (and possible higher alkanes). Their modeling applies to the late Archean-early Proterozoic. Early Archean conditions would require still higher levels to counter the even fainter sun at that time.

For the less luminous sun at 4.5 Ga, equable climate could probably be maintained at 1500 ppm CH_4 with CO_2 well above modern levels (Haqq-Misra et al., 2007). At 1500 ppm CH_4, photochemical loss of methane would be about 2×10^{11} molecules/cm^2 s (Kasting, 2005), equivalent to about 10 moles/cm^2 in a million years. The loss of methane from an anoxic atmosphere is accompanied by formation of condensable compounds that rain out into the ocean, i.e., prebiotic organic compounds (Miller, 1953, 1955). At this rate of methane destruction, a surface carbon reservoir equivalent to 20 atmospheres of CH_4 (approximately the carbon in the current near-surface carbon inventory) cycles once through the atmosphere in about 100–200 million years. Note that only a tiny fraction of this carbon is actually in the form of methane at any time, but is mainly stored in condensed organic compounds. Because the photochemical destruction of methane removes, on average, about one hydrogen from each methane molecule in making the condensed organic phases, the carbon must be cycled through the atmosphere at least 3–4 times before it is oxidized to CO_2. Note, however, that loss of reduction capacity actually depends not on methane destruction but loss of hydrogen to space. Hydrogen production from just the destruction of methane is several times the present day hydrogen loss rate (Holland, 2002), suggesting the possibility that some of this reducing capacity can be returned to the organic carbon reservoir, since hydrogen may be scavenged into condensable phases and recycled down to the surface rather than being lost. This crude calculation indicates that methane could be maintained at effective greenhouse concentrations in the early (at least prebiotic) atmosphere for up to perhaps one billion years, provided hydrothermal processes regenerate the methane from the (rained-out) oceanic carbon pool at a sufficient rate. Although this is a little short of the length of time required to maintain enough of a reduced reservoir to get to the end of the Archean, it is at least in the right range. After the first billion years biologic processes may have contributed to atmospheric methane production.

Is the abiotic production rate capable of maintaining high enough atmospheric methane levels on a prebiotic Earth? The rate of production of methane by hydrothermal activity during the early Archean is unknown, but Kasting (2005) provides some estimates for modern methane production driven by off-axis hydrothermal circulation and alteration of serpentinite that approach the modern biological methane production rate. If fluid circulation at mid-ocean ridges (or other hydrothermal systems) involved sea water containing 1% dissolved (abiotic) carbon compounds, methane production would undoubtedly be much higher than Kasting's (2005) estimate. Although there are enormous uncertainties involved in estimating likely concentrations of organic compounds in Archean sea water, hydrothermal circulation rates, and carbon compound conversion efficiencies, a calculation of hydrothermal methane production in the Archean is suggestive. Assuming a modern rate of hydrothermal sea water circulation through the crust equal to 2.5×10^{12} m^3/yr (Sleep and Zahnle, 2001), a prebiotic carbon compound concentration in sea water of 1%, and 1% conversion of the dissolved organics to methane [experimental results with modern sediments suggest conversion rates of well over 1% (Seewald et al., 1994)], methane production would be about 2.5×10^{14} g/yr. This is equivalent to about 10^{12} molecules/cm^2 s, not quite an order of magnitude higher than the present-day biogenic methane production rate (Kasting, 2005), and probably sufficient to maintain an Archean greenhouse in an anoxic atmosphere. In light of the results of Haqq-Misra et al. (2007) this would also require CO_2 levels high enough to be in conflict with geological data near the end of the Archean, and thus does not constitute an unambiguous solution to the faint young sun paradox.

Atmospheric ammonia at about 1–10 ppm as a solution to the faint young sun paradox was suggested by Sagan and Mullen (1972), but the idea was soon rejected once it became clear that photolysis removes ammonia so rapidly that its concentration would be too low (Kuhn and Atreya, 1979; Kasting, 1982). Sagan and Chyba (1997) revived the idea, proposing that UV shielding by organic aerosols derived from photochemical reactions of methane in the upper atmosphere would allow accumulation of ammonia in the lower atmosphere. Atmospheric photochemistry and climate modeling (Pavlov et al., 2001) showed that a haze layer optically dense enough to allow the requisite ammonia concentration would actually result in cooling by an ''antigreenhouse'' effect blocking visible light from reaching the lower atmosphere and surface. Haze densities low enough to limit the antigreenhouse effect allow in so much ultraviolet that biologic NH_3 generating processes [estimated at about $10^{10}/cm^2\,s$ (Pavlov et al., 2001; Zahnle, 1986)] could not maintain atmospheric concentrations sufficient for a warm climate. At present ammonia is not considered to be an important greenhouse gas in the Archean.

However, ammonia may also be generated hydrothermally from the organic products of atmospheric photochemistry (Seewald et al., 1994), a source term not previously considered. It may be that ammonia could be revived as a solution to the faint young sun paradox. Laboratory experiments on hydrothermal alteration of organic-rich sediments in contact with sea water yield NH_3 concentrations approximately equal to CH_4 concentrations (Seewald et al., 1994). Hydrothermal vent fluids have NH_3 concentrations approximately an order of magnitude lower than CH_4 concentrations, but ranging up to nearly equal concentrations. Assuming, as above, that early Archean oceans contained atmosphere-derived organic condensates subjected to hydrothermal processing, NH_3 production rates from this source might have been as high as 10^{12} molecules/$cm^2\,s$ Based on the atmospheric model of Pavlov et al. (2001), this production rate could support an atmospheric concentration of 1 ppm, even in the absence of a dense organic haze, and thus be an important contributor to the early greenhouse.

The faint young sun paradox is unresolved in spite of considerable effort over the past 20 years. Objections to high CO_2 levels based on geologic evidence remain, while atmospheric modeling indicates problems with alternative greenhouse gases. Perhaps recognition of additional source terms (e.g., hydrothermal processes) may yield atmospheric models for either methane or ammonia (or both with some elevated CO_2) that can produce adequate warming during the Archean.

7. Geology of carbon in the Archean

Geologic control on carbon systematics in the Archean is very limited, especially for the early Archean. It is very likely that there were substantial oceans and at least some pieces of continental material present in the early Archean (Wilde et al., 2001; Peck et al., 2001; Mojzsis et al., 2001; Valley et al., 2002; Harrison et al., 2005; Watson and Harrison, 2005; Nutman, 2006). The driving force for solid-Earth convection would have been at least four to eight times that at present, the latter figure assuming about half of the radioactive element inventory has since been partitioned into modern stable continental crust, and extrapolating radioactive heat production back to 4.5 Ga. These factors and Nutman's (2006) review suggest an early Earth of largely oceanic crust with (numerous?) island-arc-like belts of emergent continental crust derived from subduction, in a very active tectonic regime. Most of Earth was covered by water following early degassing. High convection rates imply equally elevated rates of ocean crust production and hydrothermal activity, at both ridges and in/near subduction zones. This is an environment in which we would expect little geologic preservation. The oldest geologic survivor of this regime, apart from individual zircon grains, is 3.9–4.0 Ga gneissic crust (Bowring and Williams, 1999), and the oldest that shows clearly preserved sedimentary affinities dates to about 3.6 Ga (Nutman, 2006). Rocks younger than 3.6 Ga are much more abundant, and record a wide array of sedimentary environments. These remnants are the major sources of geologic information concerning Earth's early volatiles. Weathering profiles in late Archean rocks (Rye et al., 1995) provide evidence concerning atmospheric CO_2 levels at about 2.8 Ga.

Massive early degassing of CO_2 has geologic consequences (Rubey, 1951, 1955; Holland, 1984; Sleep and Zahnle, 2001; Zahnle and Sleep, 2006). A strongly acidic CO_2-rich atmosphere implies spectacular weathering of exposed rocks. The production of cations by this weathering, especially calcium (and ferrous iron), should lead to massive precipitation of carbonate rocks, creating a ''storage reservoir'' for the CO_2, for which evidence is limited. Erosion *does* remove geologic evidence, and especially sedimentary rocks. However, the absence of carbonate rocks in extant Archean exposures is striking (Cameron and Baumann, 1972; Veizer, 1983; Veizer et al., 1989; Nakamura and Kato, 2002). The very early carbonates in the Isua Belt probably do not constitute an important reservoir for atmospheric CO_2 because they are metasomatic, not sedimentary, in origin (Rose et al., 1996; Rosing et al., 1996; van Zuilen et al., 2003). The crucial observation, however, is not just the paucity of carbonates, but the absence of carbonates at the same time and place that clastic sediments are present. It is difficult to believe that the clastic rocks would be preserved, without some evidence for (meta)sedimentary carbonates. Even if loss/sequestration of some carbonate (CO_2) from the surface environment is allocated to sea-floor alteration (Veizer et al., 1989; Nakamura and Kato, 2004), this does not explain the lack of carbonates in Archean sedimentary and metasedimentary rocks. Nor does subduction of possible deep-sea carbonate sediments and/or carbonitically altered oceanic crust solve the problem, because processing (heating) of the subducted crust quickly returns CO_2 to the surface. Although it is difficult to quantify the magnitude of devolatilization of subducted carbonate rocks during the early Archean, it is probable that a large fraction of the subducted carbonates (which would be at or near the upper surface of the subducting slab) would undergo enough heating at relatively shallow depth to rapidly return most of the CO_2 to the atmosphere, especially on an intrinsically hotter Earth (Sleep and Zahnle, 2001; Nakamura and Kato, 2004; Hayes and Waldbauer, 2006).

The quantitative requirement for storage of carbonate makes this even more obviously difficult. The modern near-surface inventory of carbon is equivalent to about 50 atmospheres of CO_2. Considering that CO_2 is not photochemically labile it would not be removed from the atmosphere by photochemical reactions, and ambient levels could become rather high, with all the consequences described by Rubey (1951, 1955). Converted to carbonate rocks, this amount of carbonate is equivalent to slightly more than 400 m of sediment over the entire planet. Bach et al. (2003) estimate rates of modern subduction of carbonates ranging up to 3.6×10^{13} g/yr, a figure used by Hayes and Waldbauer (2006) to estimate an important flux of carbon from the surface to the interior. Assuming current basaltic crust production rates are approximately equal to subduction rates (Hayes and Waldbauer, 2006), we can calculate present-day carbonate concentration in ocean crust as about 0.05%, or about 4 m of the total crustal thickness (as carbonates), a number also mentioned in Sleep and Zahnle (2001). Perhaps higher concentrations of carbonate in ocean crust might prevail under higher atmospheric CO_2 pressures. However, not only would average carbonate mineral contents of 5% be obvious (assuming 400 m equivalent of carbonate rocks to account for most of the CO_2), the likelihood of locally higher values, especially at shallower levels in the crust, suggests a problem for this mode of carbonate storage, unless substantial pervasively carbonatized oceanic crust is found in the Archean geologic record.

Nakamura and Kato (2004) provide evidence for extensive carbonitic alteration of *shallow* ocean crust in Archean greenstones. They find average carbonate concentrations in altered basalts in the upper 500 m of ocean crustal sections of about 5%, and estimate carbon flux into the Early Archean ocean crust of about 4×10^{13} mol C/yr. Whether this result is representative is an open question, but it does suggest the possibility of significant storage of carbonate in ocean crust. The magnitude of that storage, however, even at such high levels of carbonitization, can account for only about 10–20% of the CO_2 of a massively degassed early Earth (unless it is extended to the entire thickness of the ocean crust).

Sleep and Zahnle (2001) developed a detailed model of CO_2 cycling between the continental crust, ocean crust, and mantle, which could in principle account for depressing early atmospheric (surface) levels of CO_2. Their model is fairly complex and a complete discussion here is neither possible nor essential. Three relevant points bear on the current issue. First, although cycling of large amounts of carbonate into ocean crust and the subduction system is possible, the actual storage of CO_2 in ocean crust is limited. Second, if atmospheric CO_2 was controlled (reduced, at least initially), by cycling back into the mantle, we are left to puzzle over how the massive early degassing of volatiles (including H_2O and CO_2) can be so quickly reversed as to make the mantle a sink for CO_2. Third, as Sleep and Zahnle (2001) acknowledge, the "regassing" of the mantle by subduction must have been somewhat limited early on, when high mantle temperatures would tend to reduce the efficacy of subduction to return CO_2 to the mantle. In fact, temperatures as high as the 1300 °C needed for decarbonation reactions (Sleep and Zahnle, 2001) are clearly an overestimate, as there are many silicate-carbonate decarbonation reactions that occur at lower temperatures even at mantle pressures. And, again as noted by Sleep and Zahnle (2001), dehydration reactions of the subducted crust would provide massive amounts of water which also lead to much lower temperatures for decarbonation reactions, by lowering the partial pressure of CO_2 in the fluid phase. It is very difficult to avoid the need for a large surface carbonate reservoir (for which we have little evidence) under these conditions, even with large carbonate fluxes into ocean crust and subduction zones.

These considerations apply to the early Archean where the rock record provides little support for significant storage or precipitation of carbonate. Archean carbonate rocks become more abundant starting about 3.5 Ga (Grotzinger and Kasting, 1993), but whether these could account for the storage of enough of the early degassed CO_2 is questionable. At the other end of the Archean (ca. 2.8 Ga) weathering profiles, with an absence of siderite, indicate a relatively low upper limit on atmospheric CO_2 (Rye et al., 1995), as noted by several studies concerned with the faint young sun paradox (see above). Between these, at ca 3.2 Ga, weathering rinds on stream cobbles indicate minimum CO_2 levels a few times the present atmospheric level, still well below levels thought necessary for greenhouse warming (Hessler et al., 2004). Perhaps by the late Archean there were sufficient continental reservoirs to accommodate atmospheric CO_2 and reduce atmospheric concentrations, but carbonate reservoirs in the Early Archean remain problematical. Storage of the carbon inventory as organic compounds in the ocean does not present the same kind of problem as that for storage as carbonates, for two reasons. First, the cycling of carbon, and the reservoirs for carbon storage change dramatically through geologic time, with the gradual emergence and ultimately domination by carbonate rocks. This, and the intrinsic lability of organic carbon (especially compared to carbonates, Hayes and Waldbauer, 2006) through oxidation and biological processing, allows the destruction of a large fraction of the initial abiotic organic reservoir through time, ultimately by conversion to carbonates. These reservoir changes have consequences for the carbon isotope record, as will also be discussed below. Second, preserved organic-bearing sedimentary rocks in the early Archean are not particularly uncommon (Hayes et al., 1983; Ohmoto et al., 2005; Rasmussen, 2005).

8. Origin of life, photosynthesis and atmospheric oxygen

Holland (1984) discussed the oxidation state of the atmosphere and how it has changed through time. The biological and geological implications of oxygenation of the atmosphere and oceans are profound. This is probably the most active area of early atmospheric research, and has been for several decades (e.g., Blankenship, 1992; Catling et al., 2001; Kasting and Siefert, 2002; Lowe and Tice, 2004; Canfield, 2005; Kopp et al., 2005; Holland, 2002, 2006;).

Life is important to a discussion of the early atmosphere because primitive metabolisms may tell us about ambient conditions and because life has been a powerful agent in regulating and changing the atmosphere, and in particular the transformation to a highly oxidized surface environment. The great antiquity of life on Earth is indisputable, although a precise date of origin remains elusive. Molecular phylogeny suggests life began as early as 4 Ga, perhaps earlier (Woese et al., 1990), based on relatedness of extant bacteria, archea and eucarya. Although molecular phylogenies have been criticized as subject to errors due to lateral gene transfer (Doolittle, 1999), the general nature of the phylogenetic tree seems to be intact (Choi and Kim, 2006). The deepest parts of the phylogenetic tree are characterized by hydrogen consuming lithotrophs of archeal and bacterial lineage (Pace, 1997). This suggests ready availability of this energy source (H_2) at or near the level of the last common ancestor, although we cannot be sure of the time of origin of said ancestor. Hydrogen-based lithotrophy can be a source of carbon fixation and production of organic compounds, but cannot be a source of *prebiotic* compounds. However, recognition of a hydrogen-dependent biology may be relevant to considerations of prebiotic chemistry and the earliest atmosphere. These early organisms may point to an early Archean atmosphere especially rich in hydrogen, i.e., highly reducing.

Stromatolites and microfossils from the 3.3–3.5 Ga Onverwacht Group and the 3.5 Ga Warrawoona Group appear to be the earliest concrete evidence for life (Westall et al., 2001; Schopf et al., 2007). Although inorganic origins for these stromatolites have been proposed (e.g., Lowe, 1994; Brasier et al., 2002), morphological and paleoecological studies support an organic origin (Hofmann et al., 1999; Allwood et al., 2006). It has been proposed that carbon isotope signatures from inclusions in phosphate minerals from the Isua Group (Mojzsis et al., 1996; Rosing, 1999) indicate the presence of carbon fixing pathways even earlier, at 3.8 Ga, though this is perhaps tenuous evidence given the degree of metamorphism of the sediments and possibilities for hydrothermal processing (van Zuilen et al., 2003). Uranium-rich sediments in conjunction with ^{13}C-depleted organic material (Rosing and Frei, 2004) may also indicate early carbon fixing. It is possible that these samples date the earliest photosynthetic activity, but not necessarily oxygenic photosynthesis.

The time of origin of oxygenic photosynthesis is controversial, ranging from a minimum of 2.7–2.9 Ga based on the occurrence of 2-methylhopanes in sedimentary rocks (Brocks et al., 1999; but see Rashby et al. (2007) for a different view) and of lacustrine stromatolites (Buick, 1992), to a possible 3.5 Ga based on the earliest stromatolites (Schopf and Packer, 1987; Schopf, 1993; Hofmann et al., 1999), and finally to the speculative 3.8–3.9 Ga discussed above. Molecular phylogeny indicates an origin for oxygenic photosynthesis later than anoxygenic photosynthesis, but perhaps quite early (Pace, 1997). Even if oxygenic photosynthesis is only as ancient as 2.7 Ga, the delay in oxygenation of Earth's atmosphere until the currently generally accepted ca 2.3 Ga presents a problem if the starting atmosphere was CO_2-rich (Catling and Claire, 2005). Although a small number of dissenters (Ohmoto, 1996, 1997) defend the presence of free oxygen in the atmosphere before 2.3 Ga, most agree that prior to that time the surface environment was generally devoid of any significant amount of free O_2 (except, perhaps, for oxygen "oases" confined to geographically and/or biologically limited areas (Eigenbrode and Freeman, 2006). The 2.3 Ga date is based on the disappearance of mass-independent fractionation (MIF) of sulfur isotopes discussed below (Farquhar et al., 2000; Farquhar and Wing, 2003).

The 400 million year (minimum) gap between onset of Type II (oxygenic) photosynthesis and the rise of free oxygen requires a constraint on the productivity of the photosynthesizers. Since these are bacteria, perhaps closely related to modern cyanobacteria, they should have had doubling times on the order of a day (Mur et al., 1999), assuming no nutritional restrictions. At that rate, the fixation of carbon and consequent production of oxygen would have been so rapid that it is not even necessary to worry about sequestration mechanisms to provide for net oxygen production. Obviously this catastrophe did not occur, so there must have been some kind of nutritional deficit to keep the photosynthesizers in check. There are three obvious suspects: iron (a requirement for an enzyme in the photosynthetic chain and for nitrogen reductase) (Lehninger, 1975; Falkowski et al., 1998), nitrogen and phosphorus (Chorus and Mur, 1999). Can a shortage of any of these explain the delay in oxygenation of the atmosphere starting from a CO_2-rich atmosphere?

Iron as Fe^{2+} was freely available in the anoxic surface environment of 2.7 Ga (Cloud, 1968, 1972). Only *after* the atmosphere became oxidizing would weathering have slowed the delivery of weathered iron from uplands to coastal marine zones. The presence of abundant dissolved iron in the late Archean oceans is testified by the presence of banded iron formation (BIF), the product of oxidation of the large marine pool of soluble iron, perhaps mediated by oxygenic stromatolitic cyanobacteria (Cloud, 1968, 1972; Canfield, 2005) or by anoxygenic phototrophs (Widdel et al., 1993; Kappler et al., 2005). Even after oxidation of the atmosphere some iron would reach the coastal zone (or be recycled within that zone) where it could be mobilized by photosynthesizers under local low oxygen (organic-rich) conditions. A lack of iron cannot explain the delay in oxygenation of the atmosphere.

Nitrogen is a necessity for biological productivity, but among the major nitrogen-fixing organisms, cyanobacteria (the main oxygenic photosynthesizers) are especially prominent (Mur et al., 1999). Some accomplish this in special cells called heterocysts, while others have nitrogen fixing systems embedded within normal cells. Cyanobacteria are capable of fixing nitrogen on a "demand" basis. If there is an available source of usable nitrogen, the energy-consuming process of nitrogen fixation is depressed. Under conditions of decreased environmental fixed nitrogen, the nitrogen-fixing system "turns on". For this reason it can be difficult to evaluate the nitrogen productivity of cyanobacteria, at least globally. Estimates of current cyanobacterial nitrogen fixation span a range. If we take one reasonable (probably low-end) estimate for oceanic nitrogen fixation, we can estimate the extent to which nitrogen might limit cyanobacterial carbon fixing (and oxygen production). The current rate of oceanic biological nitrogen fixation is about 3.5×10^{13} g/yr (Bezdicek and Kennedy, 1998). Total natural nitrogen production (land and sea, including by lightning) has been estimated at about 1.85×10^{14} g/yr, more than five times the rate for just the oceans (Bezdicek and Kennedy, 1998).

Based on a C/N of 6 (in mass), this implies a potential productivity of 2×10^{14} g/yr of fixed carbon using only the nitrogen produced by oceanic bacterial nitrogen fixation, equivalent to about 5×10^{14} g/yr of O_2. The mass of oxygen in Earth's atmosphere is about 1.5×10^{21} g, suggesting that nitrogen-limited photosynthesis would take about 3 My to generate the oxygen present in today's atmosphere. However, oxygen sinks that would slow the oxidation of the atmosphere must be taken into account. These will be discussed below, once the nutrient limits are defined. Note that the current oceanic nitrogen fixing rate is well below that possible for cyanobacteria, which may fix nitrogen at rates up to $175\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$ (Chorus and Mur, 1999). This maximal rate suggests biological nitrogen fixation could be as high as 4.5×10^{15} g/yr for an Earth with a global ocean, assuming half of the oceanic area is productive.

A possible check on nitrogen availability might be a micronutrient important for the nitrogen-fixing enzyme, nitrogenase. One atom of molybdenum is needed to make each molecule of the most efficient form of nitrogenase, which also requires seven atoms of iron. Molybdenum is more mobile (accessible) under oxidizing conditions, and thus may have been less available in an anoxic surface environment (Zerkle et al., 2005). On the other hand, iron is also an essential nitrogenase component [probably the main reason iron is a limiting nutrient in photosynthesis is its role in nitrogen fixation (Falkowski et al., 1998)] and would have been readily available under the same conditions. In fact, there is also a less efficient nitrogenase that only requires iron, and which may be the more ancient form of the enzyme. A less efficient enzyme would slow the rate of nitrogen fixation in an individual cell, but would not necessarily limit overall (global) nitrogen fixation, which also depends on the population of the nitrogen fixers. Even if the doubling time for these less efficient cyanobacteria was, say, ten times that of the most efficient forms, the proliferation of bacteria would still be enormous on a short time scale. Inefficiency of other metabolic enzymes is also possible, but is answerable by the same logic. Simple inefficiency, in contrast to an absolute nutrient shortage, merely increases the doubling time, but cannot prevent an eventual "population explosion" and net productivity.

Phosphorus, which occurs in a 1/109 molar ratio with carbon in cells, is frequently a limiting nutrient in modern aquatic settings (Chorus and Mur, 1999).

Table 3. Volatiles on Earth

H_2O in hydrosphere	1.4×10^{24} g	Walker (1977)
H_2O in sediments	1.5×10^{23} g	Walker (1977)
Total C in crust	7×10^{22} g	Walker (1977), Wedepohl (1995)
Carbonate rocks in crust (equivalent C)	6×10^{22} g	Walker (1977)
CO_2 in atmosphere	4.5×10^{18} g	Walker (1977)
CO_2 production from volcanoes	1×10^{14} g/yr	Walker (1977), Hayes and Waldbauer (2006), Williams et al. (2005)
Oxygen in atmosphere	1.2×10^{21} g	Walker (1977)
Nitrogen in atmosphere	4×10^{21} g	Walker (1977)
Nitrogen in crust	1.4×10^{21} g	Walker (1977), Wedepohl (1995)
Total iron resources (mostly BIF)	8×10^{17} g	Brobst and Pratt (1973)
P in continental crust (note: ~780 ppm for both basalt and continental crust)	1.7×10^{22} g	Wedepohl (1995)
Rate of erosion of continents	$3–5 \times 10^{16}$ g/yr	Wilkinson (2005), Walker (1977)

Sizes of various surface reservoirs of volatiles and other important components on Earth, including some important rates of transfer of components significant to photosynthetic activity.

Its primary source in the surface environment is weathering of rocks. The average concentration of phosphorus in either granitic (continental) or basaltic (oceanic) rocks is about 780 ppm (Table 3). The modern average rate of erosion (and weathering) of (mostly) continental rocks of $3–5 \times 10^{16}$ g/yr gives a phosphorus delivery of $2.5–4 \times 10^{13}$ g/yr, which yields a phosphorus-limited carbon fixation rate of $1–1.6 \times 10^{15}$ g/yr, less stringent than that imposed by nitrogen fixation. At this rate the current atmospheric inventory of oxygen could be produced in about 400,000–800,000 yr.

Phosphorus sinks have been suggested as another possible limitation on photosynthetic productivity (Bjerrum and Canfield, 2002), but such sinks are not sufficient to explain the delay in atmospheric oxygenation. For example, sequestration of phosphorus on ferric hydroxide particles, although a real possibility, would not become important until after free oxygen appears. Although production of such particles in the immediate vicinity of cyanobacteria undoubtedly occurred (accompanying BIF deposition), weathering and erosion of upland areas under anoxic conditions would not produce such particles. Riverine delivery of significant phosphorus to the photosynthetically active coastal zone would continue unabated until the atmosphere itself became oxic. In addition, cyanobacteria are capable of “capturing” phosphorus during those nightly intervals when they are not actively producing oxygen (and thus inducing ferric hydroxide precipitation). Indeed, many cyanobacteria have mechanisms for phosphorus storage, perhaps driven by just that necessity (Mur et al., 1999; Chorus and Mur, 1999).

Direct inorganic precipitation of phosphorus might limit its availability to cyanobacteria, but is unlikely to have been a major factor. Phosphorus is available in many modern settings, even where it is a limiting nutrient and where inorganic precipitation may also occur. Biologic competition for phosphorus in the Archean was not what it is at present, and cyanobacteria are particularly good at competing for nutrients with other microorganisms (Mur et al., 1999). Nor were there major biological phosphorus sinks comparable to bone- and shell-forming animals. In a sense, the cyanobacteria living in shallow marine environments would have had “first call” on the phosphorus delivered by rivers.

In sum, the usual suspects for nutrient limitation cannot explain the long delay in oxygenation of the atmosphere. We are left to consider oxygen sinks large enough to consume photosynthetic oxygen during the 300–400 million year gap.

There are three major sinks for oxygen: ferrous iron in the oceans, ferrous iron and sulfur from continued weathering, and reduced carbon compounds. Ultimately, the ferrous iron in the oceans was largely deposited as iron formation as a result of oxidation (Cloud, 1968, 1972; Widdel et al., 1993; Canfield, 2005). The total amount can be approximated by the total extant iron resources, mostly in BIF (Table 3). Using this figure, the amount of oxygen consumed by this sink is about 10^{17} g. At the nitrogen-limited rate of O_2 production, this oxygen sink depletes in hundreds of years. Even if the total amount of iron formations was 100 times that currently known, this sink is inadequate to counteract potential cyanobacterial oxygen production.

Weathering releases sulfide and ferrous iron at a rate such that every 100 g of representative rock (a mix of sedimentary, granitic and basaltic) consumes about 1.5 g of oxygen (Walker, 1977). Based on the rate of erosion in Table 3, this implies oxygen consumption of $3–7.5 \times 10^{14}$ g/yr, a number that straddles the *minimal* nitrogen-limited oxygen production rate (5×10^{14} g/yr). Given that the *maximal* nitrogen-limited production of oxygen could be nearly two orders of magnitude higher, and that current non-anthropogenic global nitrogen-fixing gives an oxygen production rate more than five times higher, these numbers suggest that consumption of O_2 by weathering would slow the net release of oxygen through photosynthesis, but not by much. In any case, we are certain that photosynthetic oxygen production must exceed consumption due to weathering, not only at present, but in the late Archean, otherwise the atmosphere could never become oxic at all. Even if the excess oxygen production were as little as 10% above the weathering consumption rate, the sulfide and ferrous iron sink would be overwhelmed in thousands of years.

The consumption of photosynthetic oxygen by organic compounds is more difficult to assess. It becomes a problem *only* if there is a large initial (pre-oxygenic photosynthesis) pool of organic material that undergoes *net* oxidation once photosynthesis starts producing oxygen. Net oxygen *production* is due to conversion of CO_2 to fixed organics, that is, to production of new net biomass, whether sequestered in sediment (probably the major factor) or as additional "standing crop" (perhaps a factor when new niches open up, e.g., terrestrial plants). To the extent that biomass is recycled, with oxidation of biomass carbon to CO_2, there is no net oxygen production or consumption by biological processes. With the advent of photosynthesis, it is presumed that the availability of a large carbonate pool provides the trophic source for as much net carbon fixation as the nutrient supply allows. This is based on the ability of the first carbon-fixing organisms to rapidly proliferate up to the limits of nutrient supply, and is the basis for the preceding discussion of nutrient limits. It is not entirely necessary to consider sequestration of the new photosynthetically fixed carbon because production of this new "standing crop" of fixed carbon is a significant source of net oxygen, even without carbon burial. On the other hand one would expect this burst in productivity to be accompanied by additional carbon burial/sequestration.

If most of Earth's carbon at the initiation of oxygenic photosynthesis resides in a carbonate reservoir, the conversion of CO_2 to carbon biomass necessarily implies a comparably large release of oxygen, and rapid oxidation of the surface environment. This is the essence of the problem of the 400 million year delay in surface oxidation implicit in an early carbonate (CO_2)-rich surface environment. On the other hand, if a large fraction of the carbon is in the form of fixed carbon (or at least reduced carbon, whether abiotically or biotically produced), then our starting point is not an early CO_2-rich atmosphere/surface environment, but one in which the dominant carbon reservoir is reduced carbon compounds. As discussed in the sections on accretion and early atmosphere processes, it is conceivable to start with a reducing atmosphere that leads by obvious processes to a large abiotic reduced carbon (ARC) reservoir. Obviously, the ARC reservoir may have been modified by anaerobic biological processing before the advent of oxygenic photosynthesis, but such activity carries few, if any, implications for net oxygen production.

An ARC pool can take up a large quantity of photosynthetic oxygen. If oxygenic photosynthesis is limited by volcano-magmatic CO_2 production in the mantle (say from subducted reduced carbon compounds), we can estimate how long the oxygen freed by carbon fixation will take to oxidize the ARC pool (which perhaps originally came from atmospheric methane and/or CO/H_2). Using the current rate of CO_2 emission from volcanoes of about $6–10 \times 10^{13}$ g/yr (Walker, 1977; Williams et al., 1992) and converting it all to fixed carbon with evolution of oxygen, it would take about 2 billion years to oxidize the ARC (while preserving the photosynthetically produced carbon in sediments). This is obviously a very simplistic calculation, and no significance should be attached to the numerical result. Indeed, volcanogenic CO_2 production was probably much higher during the Archean. However, it is clear that ARC could be an important sink for photosynthetic oxygen, and also that the ARC pool could be consumed on a geologically appropriate time scale.

Nutrient limitations cannot explain the delay in atmospheric oxidation following the advent of cyanobacteria and the only oxygen sink that appears to be large enough to absorb photosynthetic oxygen production for an extended period is a large reduced carbon reservoir, which implies early Archean storage of carbon as reduced compounds rather than as carbonate. Without such a reservoir the 400 million year gap between cyanobacteria origin and atmospheric oxidation is unresolved.

A final interesting question remains: What is the ultimate source of the oxygen? There are two possibilities, either change in oxidation state of the mantle attending the conversion of reduced carbon compounds to CO_2 and/or loss of hydrogen to space. The former implies a change in upper mantle oxidation state through time. Some studies of upper mantle rocks suggest that the oxidation state (fO_2) of the upper mantle has not changed significantly since mid-Archean (Delano, 2001; Li and Lee, 2004), but other views have been expressed, including the possibility of a higher fO_2 for the early mantle (Canil, 1997). Kasting et al. (1993) provided a detailed examination of the question of the evolution of the oxidation state of the mantle and concluded that the present oxidation state may have developed from a previously more reduced state, through degassing of H_2 produced by dissociation of subducted water in the mantle. Although Kasting (pers. comm., 2007) now agrees that significant changes in mantle oxidation state are probably precluded by the petrochemical evidence, Kasting et al. (1993) provide useful insights into the magnitude of chemical interactions possible between surface and mantle, as well as the importance of hydrogen evolution at and below the surface followed by loss to space. A key point in their argument is that dissociation of water at high temperature in the upper mantle, followed by release of hydrogen from volcanoes, could result in a gradual increase in oxidation state of the upper mantle. Their model, in its most extreme version, calls for conversion of the equivalent of one-quarter of an ocean of water to hydrogen and a change in the upper mantle oxidation state from iron-wüstite to quartz-fayalite-magnetite, with a corresponding change in ferrous/ferric ratio.

In fact, the increase in oxidation capacity proposed by Kasting et al. (1993) (from dissociation of water) is just what is needed to provide oxygen to generate CO_2 from subducted ARC *without* changing the oxidation state of the mantle. Whether these two processes could have been, or were, in precise balance is less important than that they counteract one another to approximately preserve the observed oxidation state of mantle rocks. Release of CO_2 from magmatic processing of ARC and H_2 from dissociation of water ultimately results in a supply of photosynthetic oxygen once the CO_2 gets to the surface, and through loss of H_2 to space, overall oxidation of the surface. In a sense the mantle may serve as a catalytic reactor in which carbon compounds are oxidized to CO_2 and water is reduced to H_2, with both gases released to the atmosphere via volcanic emissions. This only implies that the process of oxidizing the ARC reservoir is limited by both the rate of subduction of water *and* the subduction of reduced carbon species. The release of large amounts of hydrogen to the atmosphere would have helped maintain highly reducing conditions in the atmosphere and aided regeneration of condensed reduced carbon compounds (Tian et al., 2005). Catling et al. (2001) consider a similar mechanism for oxidation of Earth's surface environment, although their emphasis is on biologic rather than abiotic methanogenesis or hydrogen generation.

9. Sulfur and carbon isotopes

The quenching of MIF of sulfur isotopes at about 2.3 Ga (Farquhar et al., 2000; Farquhar and Wing, 2003) is probably the best evidence for the transition of Earth's atmosphere to the oxidized state. MIF is thought to be due to photochemical reactions in an oxygen-free atmosphere prior to about 2.3 Ga. The history of MIF (Fig. 3) clearly reveals the sharp change at about 2.2–2.3 Ga, widely agreed to reflect a change to an oxic atmosphere, although there is evidence for some degree of MIF under modern (oxic) conditions (Pavlov et al., 2005). This profound change in atmospheric chemistry is an important geologic "boundary condition" for models of carbon cycling and atmospheric and biologic evolution.

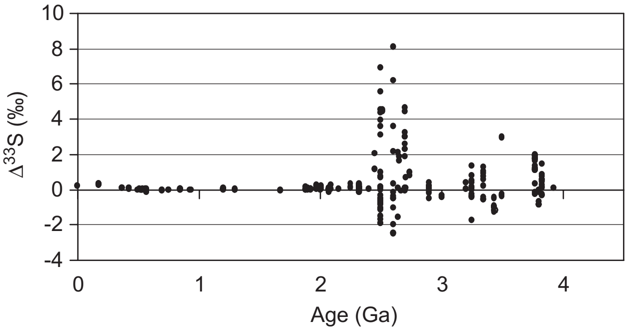

Fig. 3. Mass-independent fractionation (MIF) of sulfur through time. $\Delta^{33}S(‰) = 1000 \times [(1+\delta^{33}S/1000)-(1+\delta^{34}S/1000)^{0.518}-1]$, i.e., the deviation from ideal mass-dependent fractionation. The sharp drop in MIF at about 2.4 Ga, and essentially complete elimination of MIF by about 2.1 Ga is thought to be strong evidence for a shift to an atmosphere with significant free oxygen (data from Farquhar et al., 2000; Ono et al., 2003, 2006a, b; Papineau et al., 2005; Mojzsis et al., 2003; Hu et al., 2003; Bekker et al., 2004; Johnston et al., 2005).

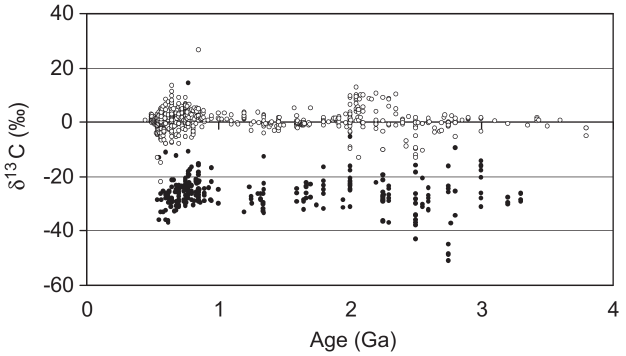

Fig. 4. Carbon isotopes through time. $\delta^{13}C$ is the fractionation of ^{13}C relative to ^{12}C compared to the PDB standard. The open circles are data from carbonate sedimentary rocks and the filled circles are data from organic-rich sedimentary rocks. Carbonate data from Shields and Veizer (2002); Organic carbon data from Strauss and Moore (1992) (no corrections have been made to the dates of Strauss and Moore).

Production of fixed carbon by photosynthesis necessarily results in changes in the isotopic ratios in the carbon pools available. Biophotosynthetic reduced carbon (BRC) is significantly enriched in the lighter isotope (^{12}C), leaving the carbonate reservoir (CC) enriched in ^{13}C (O'Leary, 1981; Schidlowski et al., 1983). Modern carbonate sediments have $\delta^{13}C = 0‰$, and carbonate sediments have varied little from $\delta^{13}C = 0‰$ since as early as 3.5 Ga (Fig. 4) (Schidlowski et al., 1983; Shields and Veizer, 2002).

The near constancy of the isotopic composition of the carbonate sediment pool is striking, especially in the Archean. Because there are links between bioorganic carbon production and deposition, carbon isotope ratios, and oxidation of the surface environment, this

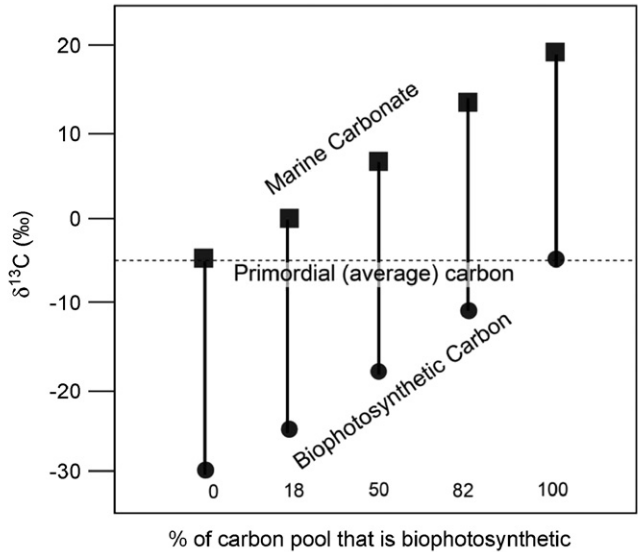

Fig. 5. Carbon isotopes and carbon reservoirs. The connected squares (carbonate carbon) and circles (organic carbon) are the $\delta^{13}C$ values for each pool in equilibrium, with the percent of the total pool as organic carbon shown as the number below each organic carbon symbol. The average $\delta^{13}C$ of the total carbon pool is the horizontal line at −5‰. The situation that applies at present (and through much of geologic history at least since 3.5 Ga) has 18% of the total carbon pool as organic carbon. Modified from Broecker (1970).

record provides important constraints on surface processes, volatile element reservoirs and atmospheric evolution.

Broecker (1970) was one of the first to recognize these links when he pointed out that for a fully equilibrated carbon system comprised of two reservoirs, inorganic carbonate (CC) and photosynthesis-based fixed carbon (BRC), the $\delta^{13}C$ of each pool is fixed by the ratio of the masses of the two pools (Fig. 5). This two-reservoir analysis, combined with the measured carbon isotope record, suggests that biogenic fixed carbon and carbonate carbon have been deposited in a ratio of about 1:4 since at least 3.5 Ga. This implies that soon after the development of photosynthesis (whether anoxygenic or oxygenic) these two carbon pools quickly, and certainly by (and since) 3.5 Ga, established an equilibrium sustaining this ratio. The mechanism that maintains this ratio is still unknown, but may have been disturbed at about 2.3 and 0.7 Ga, probably as a result of biological innovations and/or geobiological transitions.

This carbon isotope record is problematical if the prebiotic carbon pool was mainly in the form of carbonate-CO_2, as is commonly assumed. (Presumably some carbon was in the reduced carbon reservoir of prebiotic organic compounds needed to originate life, however produced (e.g., Tian et al., 2005).) Photosynthesis extracts light carbon, with net organic deposition shifting the carbonate carbon pool to heavier values. Prior to the advent of photosynthesis, carbon in every reservoir should have had primitive $\delta^{13}C = -5‰$. To get the carbonate carbon pool to $\delta^{13}C = 0‰$ (Schidlowski et al., 1983; Shields and Veizer, 2002) requires production of a biogenic carbon pool (active + geologically deposited) equal to about 20% of the total carbon pool, hence the ratio 1:4. Given our assumptions, this implies the production and sequestration of large amounts of biogenic fixed carbon by 3.5 Ga, in order that carbonates deposited at 3.5 Ga have $\delta^{13}C = 0‰$. Because we do not know when oxygenic photosynthesis began, it is possible that this early carbon fixing was entirely anoxygenic, with no implications for the oxidation state of the surface. However, if oxygenic photosynthesis was the main carbon fixing process, a biophotosynthetic carbon reservoir of this size implies the production of very large amounts of O_2, which is inconsistent with the geologic evidence for a lack of free oxygen until the latest Archean or Early Proterozoic. This may be the best evidence we have on the time of origin of oxygenic photosynthesis, that is, after 3.5 Ga.

If the starting point was a CO_2-rich atmosphere, however, even anoxygenic photosynthesis presents some problems, as there is still the need for an electron donor. If the electron (or hydrogen) donor is not water (i.e., we are not talking about oxygenic photosynthesis) there are four possibilities: H_2S, various organic compounds, Fe^{2+}, or H_2 (Lehninger, 1975). Any of these must be delivered to (or present in) the surface environment in quantities sufficient to convert a large fraction of the carbonate reservoir to fixed carbon in a comparatively short time in order to produce the requisite carbon isotope signature for sedimentary carbonate at 3.5 Ga. If Fe^{2+} was the donor, massive BIF should result, for which there is some evidence (although that is also consistent with oxygenic photosynthesis.) More problematical, the amount of iron available could not have been enough to convert the requisite amount of CO_2. If H_2S was the donor, large amounts of sulfur would have resulted. Admittedly sulfur is a rather labile species, but one might expect some evidence of massive elemental sulfur production in the rock record. An additional problem with using H_2S is its availability in an ocean with high levels of dissolved Fe^{2+}. If the donor was organic compound, a large organic compound pool is implied, and a fairly reduced surface environment. This is certainly a possibility, although it moves the conventional picture of the surface environment substantially in the direction that would result from initial degassing of reduced gases, rather than one produced by primordial degassing of CO_2. It seems unlikely that H_2 production rates would have been high enough to accomplish the necessary amount of anoxygenic photosynthetic conversion of the CO_2-rich atmosphere initially produced by large-scale degassing of CO_2 from a relatively oxidized (i.e., iron-poor) mantle. Production of copious H_2

implies that the surface carbon reservoir is ARC, rather than CO_2 or CC, as discussed in the previous section.

If we allow for the existence of a geologically deposited (sequestered) reservoir of carbonate, either sedimentary or hydrothermal or both, we can reduce the size of the rapidly mixed surface carbon pool and the necessary amount of biogenic fixed carbon. However, there are limits on the size of the geologic reservoirs. In particular, the modern platform carbonate reservoir (far and away the largest geologic carbon pool at present) was not available throughout most of the Archean. The only pool that seems available during the Archean is hydrothermally altered ocean crust. But the size of this pool is limited by the available geologic evidence to probably no more (perhaps much less) than about 10–20% of the total carbon pool (Zahnle, 2006), leaving about 80–90% in the rapidly mixed surface pool. Even with a much more carbonatized ocean crust, it would be hard to dispose of (store) enough CO_2 to get the surface pool down to a size that would eliminate our problem. Storage of early degassed CO_2 in the mantle (Sleep and Zahnle, 2001; Zahnle, 2006) is problematical, as discussed above. Current residence times of continental sedimentary carbonate are on the order of a few hundred million years or less (Walker, 1977; Garrels and Mackenzie, 1972), and would almost certainly have been less at 3.5 Ga, given the 4–8 times greater heat flow and convection rates, and a smaller volume of continental crust.

Several more detailed models have tried to deal with this carbon isotope problem. Junge et al. (1975) developed a detailed analytical treatment using a *three* reservoir model, with the third reservoir being primordial (mantle) carbon (MC). They posited an exponential decline in the mantle reservoir due to mantle degassing over time, rather than a massive early degassing event. Nevertheless, when oxygenic photosynthesis begins (in their model) at 3.3 Ga, a substantial carbon dioxide reservoir already exists. Their model shows a change in $\delta^{13}C$ for carbonate carbon from the primordial value to the modern value over a few hundred million years. They concluded that the model is consistent with the available data, but more recent data suggest otherwise (Schidlowski et al., 1983). It is possible that the ramp-up of $\delta^{13}C$ is lost in the "noise" in the isotopic record. Even without this problem, there remains the question of where the primordially degassed CO_2 (at least half of the total carbon inventory) was stored before 3.3 Ga, when photosynthesis began.

Bjerrum and Canfield (2004) formulated another explicitly three-reservoir model. They concluded that the ratio of BRC to CC can vary significantly through time without excess BRC deposition and consequent excess oxygen production, using the third reservoir (carbonation of oceanic crust, COC) to balance the carbon isotope signature. The concerns posed above about the possible size of the important COC reservoir and the rapidity of its recycling back into the surface system are yet to be answered.

The comprehensive model for carbon cycling by Hayes and Waldbauer (2006) is the most complex to date and incorporates four major reservoirs, not including the rapidly exchanging surface reservoir (their term is "exogenic") where biologic activity takes place. In addition to BRC and CC (in sediments) they include COC and a mantle reservoir (MC), as well as terms to quantify different degrees of carbon isotope fractionation between reservoirs. They also incorporate an early primordial reduced carbon reservoir due to accretion between 4.4 and 3.8 Ga, and a growth in continental storage reservoirs based on continental growth. The late-accretional reduced (abiotic) carbon pool amounts to about 15% of the total present-day surface carbon pool, and its interaction with the rest of the surface carbon pool is significant in terms of isotopic effects. The model also does not incorporate a "prompt" degassing component, such as might be due to core formation or a large impact, but does have very high rates of mantle degassing (of CO_2) that fall off approximately exponentially, similar to Junge et al. (1975). Delaying the accumulation by degassing of surface (oxidized?) carbon until 3.8 Ga makes it easier to match the carbon isotope record at 3.5 Ga without the necessity of rapid oxygenation, but it is in conflict with other models for generation of the early atmosphere (Nisbet and Sleep, 2001; Sleep and Zahnle, 2001; Zahnle and Sleep, 2002; Zahnle, 2006), especially massive early degassing.

The model of Hayes and Waldbauer (2006) is almost exhaustive in terms of different fluxes and carbon pools, and their detailed analysis is not likely to be improved upon in significant ways. Although their main arguments concern the mechanism for the carbon isotope excursion at 2.3 Ga, they provide a resolution for the problem of producing the carbonate carbon isotope signature at 3.5 Ga without concomitant oxygenation of the surface.

Although any of these models is capable of reconciling biogeologic history with the geochemical record of carbon isotopes and surface oxidation, they all do so while leaving important questions unresolved, and they do not actually investigate the full range of conditions possible, as all assume that the primary early reservoir of carbon is early degassed CO_2 with additions from continued degassing of CO_2 from the mantle. Although this is consistent with the prevailing view of the early history of Earth's atmosphere, it is possible that early degassing involved mostly reduced carbon compounds with the formation of organic carbon as the principle surface reservoir, as discussed above. Hayes and Waldbauer (2006) make a step in this direction with their significant pool of late-accreting reduced carbon,

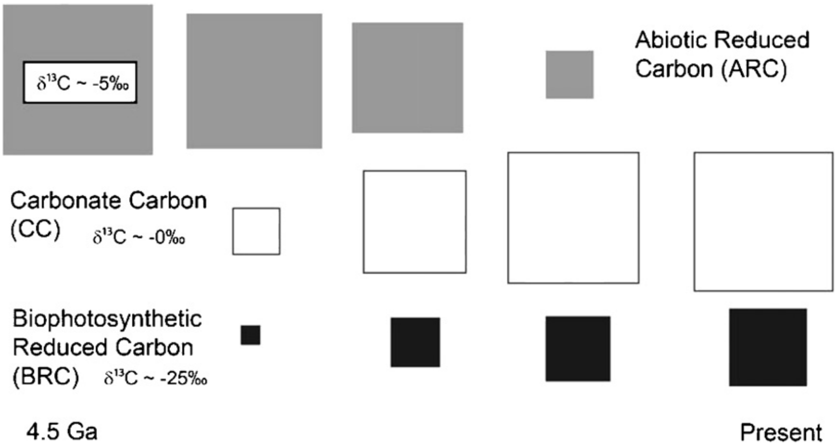

Fig. 6. A three-reservoir model for carbon isotope evolution. $\delta^{13}C$ as in Fig. 4. The initial carbon reservoir has primitive $\delta^{13}C$. ARC is slowly converted to CC by subduction and equilibration at magmatic temperatures, followed by emission from volcanoes. CC is photosynthesized (once this process evolves) and is deposited in a fixed ratio with BRC, giving fixed values of $\delta^{13}C$ for all three reservoirs. Eventually, the ARC reservoir is consumed (or nearly so), leaving CC and BRC reservoirs. It is not clear whether the ARC and BRC reservoirs will necessarily mix to a significant degree, which would change the overall $\delta^{13}C$ in the combined reduced carbon reservoir. The carbon isotope record suggests that such mixing was limited after 3.5 Ga, at least in preserved rocks.

but it may be that a model starting from an even larger reduced carbon surface reservoir would yield interesting results. A highly simplified version using a three carbon reservoir might resemble that shown in Fig. 6. Here the major initial surface carbon reservoir is ARC, the condensed material resulting from early (massive?) degassing of methane (and/or CO/H_2) followed by atmospheric photochemical processing.

Some fraction of the ARC in the Archean ocean accumulates in sea floor sediments, and some of this reduced-carbon-bearing sediment is subducted (whatever the precise nature of the subduction process at that time). Low-temperature diagenesis of the organics returns part of the subducted carbon to the atmosphere as methane (and helps maintain atmospheric levels), but some carbon reaches depths at which high-temperature (magmatic) processes convert reduced carbon to carbon dioxide (with generation of H_2). Equilibration of the *subducted* carbon with silicates at magmatic temperatures would occur in a metal-free environment. Modern degassing of CO_2-rich volcanic gases obviously takes place under similar conditions. The rate of CO_2 production depends on several factors, but at the very least is limited by the rate of subduction, and thus CO_2 levels in the surface environment can rise only slowly, and the amount of carbonate in surface reservoirs must increase slowly over geologic periods of time, consistent with Rubey's (1951) original argument.

If the dominant primordial carbon reservoir consists of ARC, such a reservoir has primordial $\delta^{13}C$ (ca. −5‰). Photosynthesis (and oxygen production) is limited by the production of CO_2 from subducted ARC even after the advent of photosynthetic microorganisms. Limitations on the rate of CO_2 production imply a limited carbonate pool that grows slowly with time, as a second surface carbon reservoir. The initial CO_2 pool has primordial $\delta^{13}C$. With the start of photosynthesis a third carbon reservoir develops based on conversion of CO_2 to biophotosynthetic carbon (BRC). This pool has a photosynthetic carbon isotope signature ($\delta^{13}C$ ca. −25‰). Extraction of this BRC pool from the carbonate reservoir shifts the CC $\delta^{13}C$ to ca. 0‰, which leads to sedimentation of the appropriate composition inorganic carbonate. Over a period of time dictated by subduction of ARC, its conversion to CC in the mantle, and return to the surface in volcanic emissions, the three reservoirs evolve with time as illustrated. The time necessary for the complete destruction of the ARC reservoir (assuming there is none left at present) is uncertain, but it could easily take a billion years or more. This model avoids the apparent necessity of quickly adjusting the carbon isotope ratio of the entire carbonate carbon pool of a CO_2-rich early atmosphere, and allows for a gradual increase in oxygen production over geologic time. As such, it somewhat resembles the model of Hayes and Waldbauer (2006), in which a reduced carbon reservoir of more modest dimensions is added by late accretion.

10. Summary

Over the last 25 years there has been considerable effort to try to resolve several outstanding questions with regard to the nature of Earth's Archean atmosphere. Geological, geochemical, paleontological and astronomical observations, biologic analysis, and modeling of atmospheres have all added to our ability to pin down timing of atmospheric "events" and to define ranges of reasonable conditions. Compared to the situation that existed when Holland (1984) reviewed the state of affairs, we certainly have more clarity, if not definitive answers.

(1) It remains clear that Earth's volatiles came from a largely cold, meteoritic source (possibly with some limited contribution from comets). The timing of accretion and the effects of late large impacts is reasonably well defined. The likely composition of accreting material has, perhaps, been better constrained based on collection of a representative(?) suite of Antarctic meteorites, probably eliminating inhomogeneous accretion as an important factor in the origin of the atmosphere.

(2) Although the prevailing view is still for an early degassed atmosphere dominated by CO_2 and N_2, the possibility for a more reduced early phase and an early surface environment dominated by reduced carbon compounds cannot be ruled out, because the precise conditions of initial degassing remain open to speculation.

(3) There is widespread agreement that a large fraction (50% or more) of Earth's surface volatile inventory degassed by about 4 Ga.

(4) Production of the essential prebiotic compounds remains difficult for a CO_2-dominated atmosphere, but a more reduced surface environment is at least a possibility that would remove this problem.

(5) Geological evidence concerning the CO_2 content of the atmosphere suggests low levels at least by the end of the Archean, and remains ambiguous, if not questionable, for the early to mid-Archean. Neither a reservoir to store CO_2, nor evidence for such storage is clear from the geological record at least before 3.5 Ga.

(6) The faint young sun paradox remains intractable, but the possibility that reduced gases may have been important continues to attract the attention of atmospheric modelers, to the extent that they are skeptical of the efficacy of CO_2 as a solution.

(7) MIF of sulfur has pinned the time of oxygenation of Earth's atmosphere at close to 2.2 Ga. This may be one of the greatest successes of the last 25 years in the field, at least in terms of precision and significance of the result. Discoveries in molecular genetics and paleontology set the origin of oxygenic photosynthesis at a minimum of 2.7 Ga, and possibly earlier. This leaves us with the considerable difficulty of explaining the delay in oxygenation of the atmosphere by 300–400 million years (at a minimum), a topic very much under discussion for the past several years. This dilemma could be removed if the major early carbon reservoir was not CO_2, but a large pool of complex organic compounds.

In general we have a better handle on most of the problems, but answers still elude us for many, if not most of them.

11. Addendum – Venus and Mars

Observations of the atmospheres of the other terrestrial planets, especially Venus and Mars, have contributed to the conventional view of CO_2–N_2 primary atmospheres for terrestrial planets, including Earth. A brief consideration (not a review) of the atmospheres (and possible evolutionary scenarios) of Venus and Mars is essential in understanding the current views of Earth's Archean atmosphere. The 100 atmosphere CO_2-rich atmosphere on Venus (Prinn and Fegley, 1987), CO_2 polar caps and the thin CO_2 atmosphere of Mars (Prinn and Fegley, 1987), and the oxidized surface of Mars all point to such compositions as being characteristic of terrestrial planets, and thus likely to be the logical primary atmosphere for Earth.

The atmosphere of Venus contains an amount of carbon comparable to the surface carbon inventory of Earth (Walker, 1977; Prinn and Fegley, 1987). If all of Earth's near-surface carbon were converted to CO_2, it would amount to about 50–100 atmospheres. It may be that a similar amount of carbon is contained in Earth's upper mantle (Walker, 1977; Sleep and Zahnle, 2001), but the numbers are close enough to suggest similar processes and origins for the carbon inventory for these planetary "twins". Note that Venus' atmosphere contains about 3 atmospheres of N_2, comparable to Earth's atmospheric and sedimentary inventory (Prinn and Fegley, 1987). Among other things, this suggests significant early volatile loss for Venus, as for Earth, perhaps due to a large impact. If so, Venus did not end up with a permanent moon, maybe for reasons proposed by Alemi and Stevenson (2006) related to the despinning of Venus. In any case it seems likely that the atmospheres of both planets are mainly due to late-accretionary additions. Venus either had an original atmosphere much like its present one, or one that was strongly reducing, as seems possible for Earth. If so, Venus must have lost enormous amounts of hydrogen to get to its current oxidized and water-poor state. H_2 loss from Venus was far higher than for Earth, both because of upper atmospheric processes accentuated by its comparative proximity to the sun, and by a much higher hydrogen mixing ratio (over an extended period) produced by vaporization of hydrogen-containing species (presumably mostly water) on a planet with enhanced (runaway) greenhouse warming. Massive hydrogen loss explains not only the lack of water, but the overall oxidized state of Venus. Walker (1977) estimates as little as 300 million years would suffice to remove an amount of hydrogen from Venus equivalent to Earth's ocean.

Mars is a much more interesting case. Hydrogen loss from Mars is easier because of the low gravity. However, lower Martian temperatures associated with its greater distance from the sun strongly suggest condensation of water and CO_2 (Walker, 1977), lower mixing ratios, and hence lower loss rates for hydrogen. This places limits on the total amount of hydrogen loss and, hence, oxidation. Lower solar flux also reduces the rate of photochemical dissociation. On the other hand, enough hydrogen loss must have taken place over several billion years to generate the oxygen to form the oxidized deposits on Mars' surface, and the surface CO_2 (if Mars started with reduced carbon compounds).

Degassing of Mars may not have been as complete as either Earth or Venus because the available accretional energy is substantially less for a Mars-sized planet (Hanks and Anderson, 1969; Walker, 1977). Nevertheless, internal heating obviously resulted in some degassing. The evidence for surface volatiles is unambiguous, both directly observed volatiles and the erosional effects that indicate past liquid (presumably water) flow on the surface (Baker, 1982, 2001). In order to account for early liquid water, Pollack et al. (1987) calculated that a 2–5 bar CO_2-rich atmosphere would be enough to increase early greenhouse warming and atmospheric pressure. Kasting (1991), on the other hand, calculated that a dense CO_2 atmosphere by itself would not be sufficient. Forget and Pierrehumbert (1997) revived the dense CO_2 model using more detailed considerations of infrared scattering by carbon dioxide clouds. However, a lack of carbonate minerals at the surface (Bibring et al., 2006) and an insufficient atmospheric loss mechanism (Barabash et al., 2007) are problems for such an atmosphere. Methane and ammonia have been suggested as additional or alternative greenhouse gases (Kasting, 1991) but have generally been rejected because of their photochemical instability, as in the case of Earth, as discussed above.

If we accept that large amounts of water once at Mars' surface are now concealed below the surface, such a water reservoir must also contain carbon compounds, either in reduced or oxidized form. We do not have very good constraints on the volatile inventory of Mars, so it is difficult to quantify reservoir sizes. The erosional surface features suggest large fluid flows (both water and ice), but provide limited information about total fluid volumes, although a water layer equivalent to about 1 km has been suggested (McKay and Stoker, 1989). The available topographic sinks for fluid on Mars (especially the northern plains) could accommodate a substantial Martian "ocean".

If Mars is modeled with an early reduced atmosphere and surface, we get some interesting results. The constraints that any such model must match include, in addition to a highly reduced starting point:

(1) presence of large amounts of fluid (mainly water?) at the surface for an extended period,
(2) sequestration of that fluid (out of sight) well before the present era,
(3) production of climate conditions conducive to surface aqueous fluid early in Mars' history in spite of the faint early sun, and perhaps episodically since,
(4) change in climate conditions to colder planetary temperatures, as at present, in spite of increasing luminosity of the sun,
(5) production of CO_2 to make the present atmosphere and polar caps,
(6) oxidation of the surface.

The following scenario fits all of these requirements.

Degassed water was accompanied by reduced gases such as methane and ammonia, perhaps in amounts approximately proportional to those on Earth. Photochemical processing of this reduced atmosphere destroyed both the methane and ammonia, albeit somewhat more slowly than on Earth, but still rapidly in geological terms. This resulted in an organic-rich water ocean, as on Earth. The presence of organics in solution allowed the ocean to remain liquid even at temperatures somewhat below the normal freezing point of water (the same phenomenon may have occurred on Earth). On the other hand, continued hydrothermal activity in the presence of an organic-rich ocean regenerated methane (and maybe ammonia) to give atmospheric concentrations high enough to provide a warm climate even without freezing-point depression in the ocean. This suggestion for generating methane is similar to the one made (Lyons et al., 2005) to provide a non-biogenic source of the methane recently discovered in Mars atmosphere (Mumma et al., 2004, 2005; Krasnopolsky et al., 2004; Formisano et al., 2004).

Hydrothermal activity may have been due to volcanic centers or perhaps to early plate-like tectonic activity. Mars may exhibit (now extinct) plate-like processes, although it is now considered to be a one-plate planet (Luo and Stoddard, 2002). In any case, the vigor of volcano-hydrothermal processes on Mars decreased substantially with time, as it must on any planet. Because Mars is small compared to Earth, the cooling of the planet and fall-off in hydrothermal activity took place more rapidly than for Earth and may be essentially extinct at present.

During the interval when hydrothermal regeneration of methane (and ammonia?) produced enough greenhouse effect to moderate the climate, liquid water was possible on the surface, due to the combination of greenhouse enhanced temperature, increased atmospheric pressure, and freezing-point and vapor pressure depression from dissolved organics (and inorganics). Under these conditions a more or less normal hydrologic cycle was maintained. With waning hydrothermal activity, the rate of regeneration of methane could not keep up with photochemical destruction, leading to gradual loss of greenhouse warming. At some point climate deterioration led to freezing of the oceans and termination of a normal hydrologic cycle, with perhaps intermediate episodic ''ice-age-like'' climate oscillations. Windblown sediment covered the frozen oceans. Continued loss of hydrogen from atmospheric water, and near-surface water bleeding slowly into the atmosphere, provided oxygen to oxidize iron in surface materials and oxidize remaining surface carbon compounds to CO_2. (Some CO_2 undoubtedly also formed as a consequence of H_2 loss during the era of liquid surface water.)

The current state of Mars matches this model. The Martian oceans are frozen beneath a (thin?) coating of oxidized sediment. They probably have a significant content of organic compounds as well as inorganic salts. The climate is cold enough that most of the CO_2 is in the form of polar caps, but CO_2 cycles seasonally through the atmosphere. Surface atmospheric pressures are too low to sustain liquid water at the surface. Methane emissions are small but detectable, and may be driven by minor remnant hydrothermal centers.

This model suggests predictions concerning Mars. First, the buried frozen oceans should contain significant amounts of organic compounds. Second, the oxidation so obvious in surface views of Mars may be just that: *surface* oxidation. There should be large quantities of organic compounds not far below the oxidized veneer. This organic material may be accessible by a very modest amount of excavation. It is possible that the dark ejecta associated with recent small cratering events (Malin et al., 2006) may be due to organics. Oxidation of such deposits might explain the observed changes in newly exposed surfaces with time (Malin et al., 2006), since any reduced carbon compounds exposed at the surface (e.g., by impacts) would be fairly rapidly oxidized. Finally, if life has arisen on Mars it probably did not evolve methanogensis. Methanogenic bacteria, provided they had sufficient nutrients, should have been able to compensate for the decrease in hydrothermal methane production and maintain an equable climate. Clearly this did not happen. Other (probably bacterial?) life is possible on Mars, but given the primitive/ancient nature of methanogenesis on Earth (Ueno et al., 2006), Martian life should be (have been?) very primitive, indeed. It may be that relaxing our view of the initial atmospheric composition of Mars to include the possibility of a highly reducing surface environment may provide a possible answer to the question: ''What was a 'wet and warm' early Mars really like?'' (Kerr, 2008).

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