Processes on the Young Earth and the Habitats of Early Life

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Annu. Rev. Earth Planet. Sci. 2012. 40:521–49

The *Annual Review of Earth and Planetary Sciences* is online at earth.annualreviews.org

This article's doi:
10.1146/annurev-earth-042711-105316

0084-6597/12/0530-0521$20.00

Keywords

Hadean, Archean, komatiites, photosynthesis, crust

Abstract

Conditions at the surface of the young (Hadean and early Archean) Earth were suitable for the emergence and evolution of life. After an initial hot period, surface temperatures in the late Hadean may have been clement beneath an atmosphere containing greenhouse gases over an ocean-dominated planetary surface. The first crust was mafic and it internally melted repeatedly to produce the felsic rocks that crystallized the Jack Hills zircons. This crust was destabilized during late heavy bombardment. Plate tectonics probably started soon after and had produced voluminous continental crust by the mid Archean, but ocean volumes were sufficient to submerge much of this crust. In the Hadean and early Archean, hydrothermal systems around abundant komatiitic volcanism may have provided suitable sites to host the earliest living communities and for the evolution of key enzymes. Evidence from the Isua Belt, Greenland, suggests life was present by 3.8 Gya, and by the mid-Archean, the geological record both in the Pilbara in Western Australia and the Barberton Greenstone Belt in South Africa shows that microbial life was abundant, probably using anoxygenic photosynthesis. By the late Archean, oxygenic photosynthesis had evolved, transforming the atmosphere and permitting the evolution of eukaryotes.

INTRODUCTION

Ga: billion years

Gya: billion years ago

Our image of the early Earth has changed greatly over the past two decades, with important consequences for models of the origin and early evolution of life. **Figure 1** shows two contrasting views of the surface of earliest Earth. In the 20-year-old image in panel *a*, we see a Hell-like, Hadean landscape of fiery volcanoes beneath a menacing red sky; the more recent image in panel *b* shows luxuriant microbial colonies on a tranquil beach. What caused this dramatic change in our vision of the young Earth?

The discovery of >4-Ga-old (>4-billion-year-old) zircons (Cavosie et al. 2005, 2007; Froude et al. 1983; Wilde et al. 2001) radically changed our interpretation of the first part of Earth's history. The zircons, found first in Mount Narryer and then in Jack Hills, both in Western Australia, have ages from approximately 3.1 Ga (that of the quartzitic metasediment from which they were extracted; Kinny et al. 1990) to just over 4.4 Ga (Wilde et al. 2001). The latter age is some 150 million years less than accretion at 4.56 billion years ago (4.56 Gya), and merely 100 million years after the impact of the planetesimal Thea that led to the formation of the modern Earth-Moon system and the start of the Hadean (Goldblatt et al. 2009, Halliday 2003).

Zircon is ubiquitous in granite but rare in rocks of more mafic compositions. The compositions of the >4-Ga-old zircons are similar to those in modern granitoids (Maas et al. 1992, Mojzsis et al. 2001). Thus, this mineral provides evidence for the existence of granite >4 Gya. Because granitoids define the continents, it follows that some felsic crust had already formed at this early stage of Earth's history. Campbell & Taylor (1983) noted that, on the modern Earth, granite forms in abundance only when hydrated basaltic crust is subducted.

Oxygen isotopic analysis of the old zircons supports the inference by Campbell and Taylor. Cavosie et al. (2005) and Mojzsis et al. (2001) reported significant fractionation of oxygen isotopes in the minerals dating from >4 Gya—the oldest zircon they measured has a $\delta^{18}O$ of +4‰, a value

Old concept of the Hadean Earth | **Updated reconstruction**

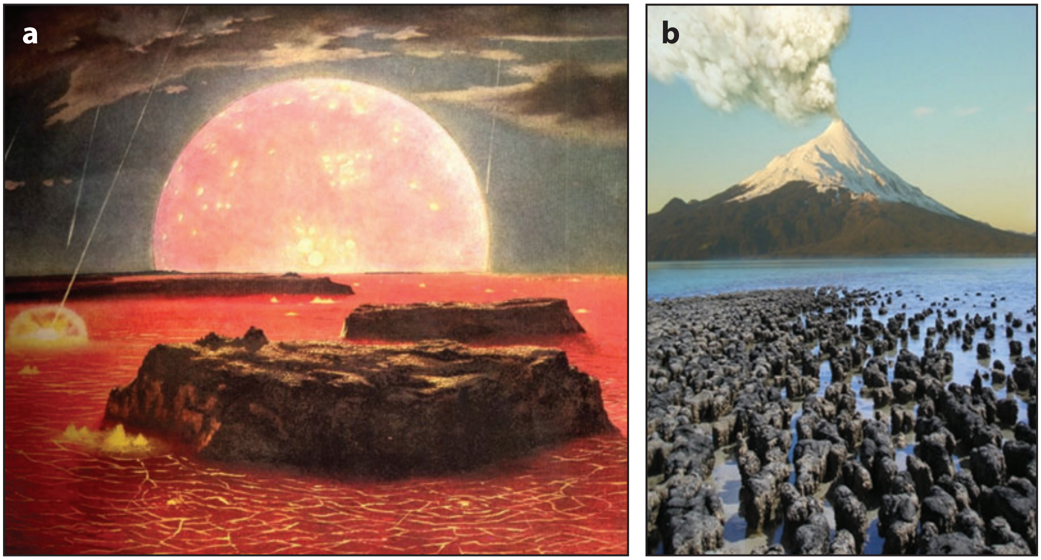

Figure 1

Two views of the young Earth. (*a*) Image reflects the old idea that the Hadean was Hell-like, covered by lava and impacted by meteorites. (*b*) A more recent image shows oceans and primitive life (from **http://archenv.geo.uu.nl/**).

implying that the source of the granite was processed at low temperature, as could have happened only at the cool surface of Earth. Comparison with compositions of modern granites suggested that Hadean granitoids—the inferred source of the Jack Hills zircons—contained a sedimentary component. Because most sediment forms through fluvial erosion, conditions at Earth's surface at the very start of its history were cool and clement (Hren et al. 2009, Ushikubo et al. 2008, Valley et al. 2002).

Analysis of radiogenic isotopes in rocks derived from the terrestrial mantle provides a record of very early differentiation of the interior of Earth and indicates that material enriched in incompatible elements had segregated within a few hundred million years of accretion, leaving portions of this mantle depleted in these elements (Bennett et al. 1993, Boyet & Carlson 2005, Caro et al. 2005, Galer & Goldstein 1990, McCulloch & Bennett 1994). Before the Jack Hills discovery, peering into the gloom, we imagined a Hadean Earth similar to the first image in **Figure 1**: a planet covered by lavas and impact breccias, and blanketed by a primitive Jupiterian atmosphere. The Jack Hills zircons changed our ideas to such an extent that we now imagine that continents and oceans existed at that time. Furthermore, if there were water and if temperatures were moderate, it is only a small step to imagine that life emerged much earlier than previously thought possible on the surface of the Hadean planet (Nisbet & Sleep 2001, Russell & Arndt 2005).

In this article, we review current ideas about how Earth functioned in the first part of its history. We focus on issues that excite all those who work in the field. The most pertinent are listed below:

- Temperatures in the Archean mantle
- Archean geodynamics—plate tectonics or something else?
- The volume of the Archean continental crust and the mechanism of crustal growth
- The faint young sun paradox
- The temperature and composition of the oceans
- The origin and evolution of life
- The coevolution of the atmosphere and biosphere in the Archean

TEMPERATURES IN THE ARCHEAN MANTLE

The Archean mantle is commonly thought to have been somewhat hotter than the modern mantle (see Nisbet et al. 1993; for more recent studies, see Benn et al. 2006, Brown & Rushmer 2006). All sources of internal heat—radioactivity, exothermic core crystallization, and the release of residual heat from accretion—were far greater then than they are now. Richter (1988) and Franck (1998) calculated that the rate of heat production was three to six times higher 4 Gya. This led them to suggest that mean mantle temperatures were 400–500°C greater. Higher temperatures would have greatly decreased the viscosity of the mantle, implying more vigorous convection or perhaps a different style of convection (Davies 2007, Jaupart et al. 2007, Jaupart & Mareschal 2010).

The consequences of greater heat production are much debated. One possibility is that more vigorous convection led to rapid movement of small tectonic plates or to larger, more abundant, and more vigorous mantle plumes (Bickle 1978, Condie & Benn 2006, van Kranendonk 2010). An alternative view is that accelerated convection resulted in more efficient transfer of heat to the surface and that this transfer buffered internal temperatures to values only slightly greater than those in the modern mantle (Labrosse & Jaupart 2007). Overturn of the accumulated layers of a nearly solidified magma ocean may also have resulted in rapid evacuation of heat (Kramers 2007), or the formation of a strong depleted lithosphere could have modulated the vigor of convection through most of the Hadean-Archean (Korenaga 2006).

Evidence about Archean mantle temperatures is difficult to find. The most direct source of information is the record of eruption temperature of komatiites, which petrologic, mineralogic, and experimental studies have shown is several hundred degrees higher than that of modern basalts (Arndt et al. 2008, Herzberg et al. 2006, Nisbet et al. 1993). An alternative viewpoint advocated by Grove & Parman (2004) is that komatiite is relatively cool hydrous magma that formed in the Archean subduction zones. Recent work (e.g., Berry et al. 2008) casts doubt on this wet-mantle interpretation (see discussion in Arndt et al. 2008).

If komatiites were produced by melting in mantle plumes (Arndt et al. 2008, Campbell et al. 1990, Dostal 2008, Herzberg 1995), their temperatures provide evidence only that the temperature of these plumes was unusually high; they provide no direct record of the temperature of the ambient mantle. From fluid dynamic arguments and inferences about the physical properties of mantle rocks, we infer that the temperature difference between the plume and normal mantle cannot have been more than a few hundred degrees (Farnetani 1997, Farnetani & Richards 1994, Herzberg & Gazel 2009), but the exact figure in uncertain. To obtain more reliable information about ambient mantle temperature, we need to consider the composition of basalts, the most common rock in Archean greenstone belts.

Abbott et al. (1994) showed that Archean basalts have higher MgO contents, and thus higher temperatures, than their modern equivalents. However, almost all basalts are evolved magmas produced by fractional crystallization of primary mantle melts (O'Hara 1968) and it is difficult to extract information on source conditions from such evolved melts. Another approach is to use a combination of major and trace elements. Arndt et al. (1997) showed, for example, that Archean basalts contain the unusual combination of low contents of incompatible trace elements (which imply high degrees of melting) and high iron contents (which imply melting at great depth). The only way to produce this combination is if the mantle source intersected the peridotite solidus at depth, a situation that arises only if the source is relatively hot. The implication is that temperatures in the ambient mantle in the Archean were indeed higher than those of the modern mantle.

A puzzling aspect of the composition of komatiites is an apparent lack of secular change of their MgO contents: As shown in **Figure 2**, the maximum MgO, and thus the maximum source temperature, is essentially the same in examples from 2.7 Gya and those from 3.5 Gya. Jaupart & Mareschal (2010) and Herzberg et al. (2010) provide an alternative view of the long-term change in mantle temperature. There is no doubt that the mantle was extremely hot—indeed, largely molten—immediately after the Moon-forming impact of 4.5 Gya, but it is probable that vigorous convection in the magma ocean, or massive overturn at the late stages of solidification (Elkins-Tanton 2008), rapidly evacuated the heat, leaving the planet relatively cool (Abe 1997). Only later did radioactivity and transfer of heat from the core cause the mantle to heat up again. The estimate of temperature variation by Korenaga (2008a), traced in **Figure 2**, agrees qualitatively with that defined by the volcanic rocks. The implication is that the temperature of mantle-plume sources of komatiite reached a maximum in the mid-Archean then slowly declined. Ambient mantle temperatures in the sources of basalts were several hundred degrees lower, but they may have followed a similar path, also reaching a maximum in the mid-Archean (Herzberg et al. 2010, Korenaga 2006, Labrosse & Jaupart 2007).

TEMPERATURES AND STRUCTURE OF ARCHEAN CONTINENTAL CRUST

The continental crust had greater heat production than it does today, given the greater abundance of heat-producing isotopes in the early part of Earth's history. The major-element compositions of Archean granitoids are generally similar to those of modern granitoids (Condie 1993, Martin 1994), and they typically contain somewhat lower contents of heat-producing elements such as potassium, thorium, and uranium. The concentrations of short-lived, heat-producing isotopes,

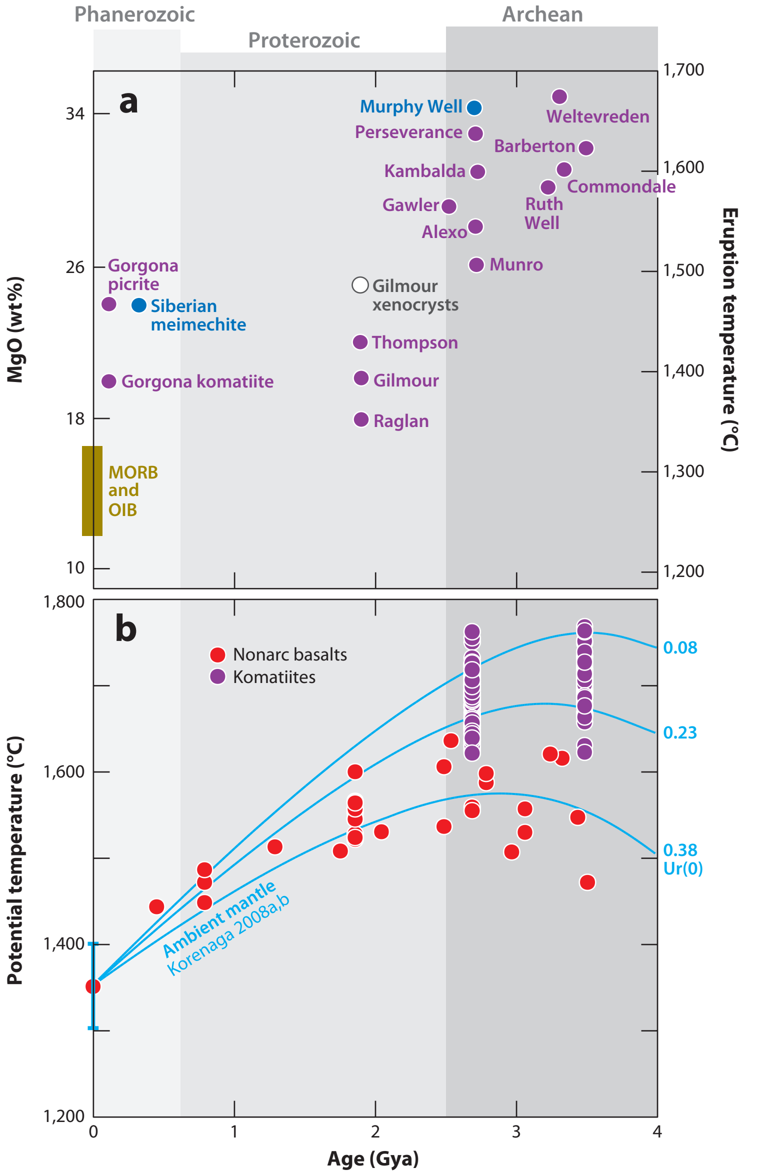

Figure 2

Variation of mantle temperature through time. (*a*) MgO contents and eruption temperatures of komatiites. The temperatures are calculated using the relation T(°C) = MgO*20 + 1,000 from Nisbet (1987) and assuming that komatiites are anhydrous. Siberian meimechites and Murphy Well komatiites (*blue*) contain a significant proportion of water and/or CO_2 and erupted at lower temperatures than the others. Abbreviations: MORB, mid-ocean ridge basalt; OIB, ocean island basalt. From Arndt et al. (2008). (*b*) Estimated potential temperatures of komatiites and nonarc basalts. The blue lines show estimated temperature variations through time. These cooling curves are calculated using various Urey ratios covering the plausible range of the present-day value Ur(0). From Herzberg et al. (2010).

however, were far higher and radioactive decay of these isotopes heated Archean granites to close to their melting points.

Kamber et al. (2005) and Kamber (2007) quantitatively estimated heat production within the Archean continental crust and concluded that the rate was three to four times greater than in the modern crust. In their opinion, before approximately 3.5 Gya, the crust was "thermally unstable," meaning that the temperature in much of the crust would have exceeded the granite solidus, a situation they consider unrealistic. Instead, they propose that the crust before 3.5 Gya was basaltic. An alternative interpretation, which we prefer, is that the crust before 3.5 Gya underwent near-continuous partial melting and that the magma ascended to the surface, taking heat with it. Efficient "sweating" and advection of heat would have kept the deep crust near its solidus, but not necessarily making it unstable.

The hot Archean continental crust would have been very ductile, easily deformable and unable to sustain the loads exerted by high mountain ranges (Rey & Houseman 2006). Although its average thickness would have been about the same as modern crust, deep crustal roots would have been absent. With more subdued topography and in the presence of more voluminous oceans (discussed in the following section), much of the Archean crust could have been flooded (Arndt 1998, Flament et al. 2008). Below the crust, the evidence for significant regions of thick continental lithosphere provided by diamonds in Witwatersrand sediments (Nisbet 1987) indicates the lithosphere had cooled over several hundred million years.

TEMPERATURES AT THE SURFACE

Knauth & Lowe (2003), Knauth (2005), and Robert & Chaussidon (2006) used isotopic evidence from Archean cherts to infer a hot climate with ocean water perhaps as warm as 50–70°C. Very high temperatures raise interesting questions: First, the most likely way to sustain warmth would have been a potent methane greenhouse, implying a strong source of biogenic methane. There is now much good C isotopic evidence for mid-Archean methanogenesis (e.g., Grassineau et al. 2006), but was the source capable of sustaining a 70°C greenhouse? Second, a very hot ocean would imply massive evaporation. On the modern Earth, this would bring extreme weather (intense cyclones). The mid-Archean sedimentary record shows no obvious sign of unusually abundant tempestite deposits. However, on a cloudy Archean planet with limited land masses and a mostly oceanic surface, were there very small pole-to-equator temperature differences, rendering the climate a steady downpour rather than a procession of fierce typhoons? Third, a hot ocean would partition water high into the atmosphere with a weak atmospheric cold trap. Could this lead to increased high-altitude photolysis and enhanced loss of hydrogen into space ejected by radiation in the uppermost atmosphere?

This interpretation of the oxygen isotopic record of marine Archean cherts depends, however, on the extent to which the analyzed samples of chert represent chemical precipitates from seawater and not from heated hydrothermal fluids (Marin et al. 2010). In addition, if the oxygen in seawater during the mid-Archean were significantly lighter than it is today, the inferred temperatures would be much lower and closer to modern values. Blake et al. (2010) used phosphate oxygen isotopic evidence from Barberton to suggest that ambient Archean surface ocean water was in the 26–35°C range, comparable to modern tropical values. This debate continues.

THE VOLUME OF THE OCEANS

Persuasive arguments indicate that the volume of the oceans in the Archean was greater than that of today (Bounama et al. 2001, Lecuyer et al. 1998, Sleep et al. 2011). Water is cycled continuously through the modern mantle. The cycle starts with degassing of magmas as they erupt at mid-ocean ridges, oceanic islands, and island arcs via a process that feeds water and other gases into the atmosphere and hydrosphere. The cycle continues with hydration of basaltic rocks of the oceanic crust at mid-ocean ridges, and it terminates with subduction of this hydrated crust back into the mantle. Some of the water cycles deep into the mantle, but most is liberated during dehydration of altered oceanic crust.

The moderator of this cycle is the formation of hydrous minerals at low temperatures in the oceanic crust and the destabilization of these minerals as temperatures increase within the subducting slab. In the hotter Archean mantle, these reactions took place at shallower depths and may have operated more efficiently. Hotter magmas degassed more completely, and more effective dewatering of the subducted slab would have meant that, compared with today, less water was cycled back into the mantle: The mantle would have been drier than it is now, with a greater volume of water partitioned to the surface.

Throughout Earth's history, but particularly during early stages when atmospheric temperatures were greater, hydrogen has escaped from the atmosphere into space, thus leaving oxygen. If the rate were greater than ongoing volatile accretion from meteorites and "snow" from space, Earth would have had a net loss of water (Catling et al. 2001, Lecuyer et al. 1998, Sleep et al. 2011). The inference is that the Archean ocean volume may have been larger than today (perhaps as much as twice as large). More voluminous oceans would have flooded a greater proportion of the continental crust (Arndt 1998, Flament et al. 2008). In other words, even if the volume of continental crust has been roughly invariant, the extent of emerged land in the Hadean and Archean may have been significantly less than is present today.

ARCHEAN GEODYNAMICS: PLATE TECTONICS OR SOMETHING ELSE?

Providing a key insight into Archean geology, Sleep & Windley (1982) noted that the degree of melting of mantle upwelling beneath a mid-ocean ridge depends on the temperature of the source: Hotter mantle yields a greater volume of melt, and because the rate of mantle upwelling beneath a mid-ocean ridge is linked directly to the rate of plate divergence, the magma from hot mantle erupted at the surface to form thick oceanic crust. Sleep & Windley (1982) also estimated that the Archean oceanic crust was 20 km thick, some two to three times greater than modern oceanic crust. This crust would likely have been more magnesian than modern crust, and it differentiated into a thin upper layer of evolved basalt and a thicker layer of plagioclase, pyroxene, and olivine cumulates. The underlying lithospheric mantle consisted of strongly depleted harzburgite. Because the dense garnet component of the original mantle peridotite had been extracted in outgoing melts and transformed to less dense plagioclase in the crystallized basalt, the intrinsic density of the Archean lithosphere was probably less than that of the modern lithosphere.

This leads to the hypothesis that the Archean lithosphere would have been relatively buoyant. If this buoyancy prevented subduction, then another type of convection must have cooled the mantle and a nonplate mechanism may have cycled material to and from the surface. If we accept this line of reasoning, another process, such as "sagduction," in which granitic magma results from melting at the base of overthickened piles of basalt or within downward dripping diapirs (Bédard 2006), may have produced the abundant granites that intruded through the Archean.

It is not clear, however, that thick oceanic crust prevented subduction. Note also that the deeper parts of the thick oceanic crust would have transformed into blueschist or mafic granulite as it cooled, thus increasing density, and into thick eclogites on subduction. If the Hadean asthenosphere were hotter than it is today, it would have had lower viscosity and would have been less dense and far less viscous: As such, subduction would be easier.

Two hypotheses for the mechanism of Hadean and Archean subduction depend on extraction of high-degree partial melts having produced a highly refractory upper mantle. Korenaga (2006) accepted that the upper oceanic layer was thick but calculated that its high viscosity and low density resisted, but did not prevent, subduction. Davies (2007) suggested that partial melting of the refractory upper layer beneath mid-ocean ridges produced only a small volume of melt: This would have erupted to form crust that was little thicker than modern oceanic crust. Both suggestions obviate the need to search for an alternative origin of granite.

THE VOLUME OF ARCHEAN CONTINENTAL CRUST AND THE RATE AND MECHANISM OF CRUSTAL GROWTH

Much debates focuses on the growth rate of continental crust. Many isotope geochemists believe that the volume of crust remained small for the first billion or so years and that continent growth began in earnest only at the end of the Archean (Albarède 1998, Coltice et al. 2000, Kramers 2007, Reymer & Schubert 1984, Taylor & McLennan 1985). In contrast, Armstrong (1981) proposed that the crust grew rapidly during the first 500 million years of Earth's history and reached its present volume as early as 3.8 Gya. Thereafter, net transfer of granitic material from the mantle to the surface (continent growth) was balanced by the return of material to the mantle (crustal recycling). Arguments for and against the two interpretations are summarized in **Table 1**.

New dating of crustal rocks has revealed regions of unexpectedly old crust in various parts of the world. The oldest rock in the world is the Acasta Gneiss in northern Canada dating from approximately 4 Gya (Bowring & Housh 1995). More recent studies of the Nuvvuagittuq (Porpoise Cove) region, also in Canada, have provided Nd isotopic evidence that this series of 3.8-Ga-old metavolcanic and metasedimentary rocks was derived from still older (>4 Gya) continental crustal rocks (O'Neil et al. 2007). Finally, the crucial discovery of zircons from >4 Gya, reinforced by the relicts of the crust in the Acasta Gneiss (Iizuka et al. 2007) and elsewhere, further supports the Armstrong model.

Some sort of stable platform was necessary for zircons to have survived for more than a billion years at the surface of the Hadean-Archean Earth, from the time they initially crystallized, through periods of repeated reworking, to the time of deposition of the sediments at approximately 3.1 Gya (Wilde & Spaggiari 2007). Mafic crust is prone to subduction; the only permanent and stable construct at the surface of Earth must have been similar to modern continental crust underlain by low-density refractory continental lithosphere (Griffin et al. 2003).

However, can the crust that contained the parental granites of Jack Hills zircons truly be considered the equivalent of modern continental crust? And was its volume similar to that of modern crust at the start of the Archean, as in the Armstrong model, or was it far less? Many authors (e.g. Moorbath et al. 1986, Kamber et al. 2005) argue that the presence of a few zircons in only one small part of Western Australia, and their virtual absence from almost all other regions of old crust, indicates that the volume was small. Our alternative point of view is that it is remarkable that any material survived at Earth's surface for its first billion turbulent years and that minimal survival of such material is to be expected. The total surface area of the Acasta Gneiss outcrop is a few tens of square kilometers—was this the total extent of the Acasta continent, or has most of this continent been totally destroyed or had its isotopic clocks reset so that no evidence of its antiquity was preserved? We find the latter interpretations more reasonable.

New data issuing from U-Pb and Hf isotopic analyses of old zircons reveal, however, that the process that produced the Jack Hills granites was very different from that which operates

Table 1 Argument for and against two competing models for the rate of growth of continental crust

Continuous crustal growth model	Armstrong's early growth model
Little continental crust was present before ~3.8 Gya; it then grew continuously, though perhaps episodically, through geological time	Continental crust grew rapidly and had reached the modern crustal volume by ~3.8 Gya; thereafter, recycling to the mantle balanced crustal growth
Continental crust older than ~3 Ga is scarce; crust older than 4 Ga is unknown	The probability of survival of crust decreases with age; old crust is either recycled to the mantle or the isotopic record is reset. Recent discoveries show that old crust is more abundant than previously thought
Pre-4-Gya zircons are very rare (Jack Hills/Mt. Narryer is exceptional). They are absent from most granitoids and sediments prior to 3 Gya	The probability of survival of zircons dating from 4 Gya is very low. New discoveries in North America (Acasta, Wyoming) broaden the known distribution of Hadean zircons
Most granitoids and sediments prior to 3 Gya contain no isotopic record of older crustal precursors	Older continents are not necessarily recorded in younger sequences (e.g., Birimian, Boher et al. 1992). Hf isotopes in zircon record crust from 4 Gya in Africa, North America, China, and Australia (Pietranik et al. 2010, Nebel-Jacobsen et al. 2010)
Isotopic evidence rules out massive sediment subduction; no other effective mechanism of recycling continental crust to the mantle exists	Cycling of lower continental crust into the mantle is demonstrated by ultrahigh-pressure assemblages and tectonic reconstructions of continent-continent collisions
Critical trace-element ratios such as Nb/U or Nb/Th are mantle-like in volcanic rocks prior to 3.5 Gya, but younger rocks record evidence of the presence of crust or of crust extraction	Ratios including mobile elements such as U and Th are unreliable; high magma flux from the deep source plume sources may be unaffected by crust extraction
Models combining trace-element and isotope data predict little crustal growth before ~3.8 Gya; Ar isotopes predict little crustal growth before ~3.8 Gya	Nd (143 and 142) and Hf isotopes provide evidence that extraction of enriched material before 4 Gya produced depleted mantle (e.g., Galer & Goldstein 1990, Bennett et al. 1993, McCulloch & Bennett 1994, Boyet & Carlson 2005, Caro et al. 2005). The material was most likely continental crust; its presence in sequences from four continents indicates that this crust was widespread
Freeboard arguments suggest an early unimodal hypsographic curve, with very few source regions for quartz-rich or aluminosilicate clastic sediments	Bimodal hypsographic curve present early in Earth history. Voluminous oceans imply isostatic equilibrium with thick continental crust (Hess isostatic relationship). Early on, there would be some source regions delivering terrigenous clastics

in modern subduction settings. The ancient zircons plot on a trend in an ε_{Hf} vs time plot (**Figure 3**) that reveals a record of repeated reprocessing of an enriched source material. Kemp et al. (2010) proposed that the source was mafic crust that was repeatedly remelted, with little to no introduction of juvenile magma from the underlying mantle. This pattern differs from that in modern subduction zones, where juvenile input is normally seen. Remelting was possible in this early crust because it contained high concentrations of heat-producing isotopes that kept the newly produced granite close to its melting point. The mafic crust probably formed a stagnant lid beneath which the mantle convected but contributed little new magma to the site of melting.

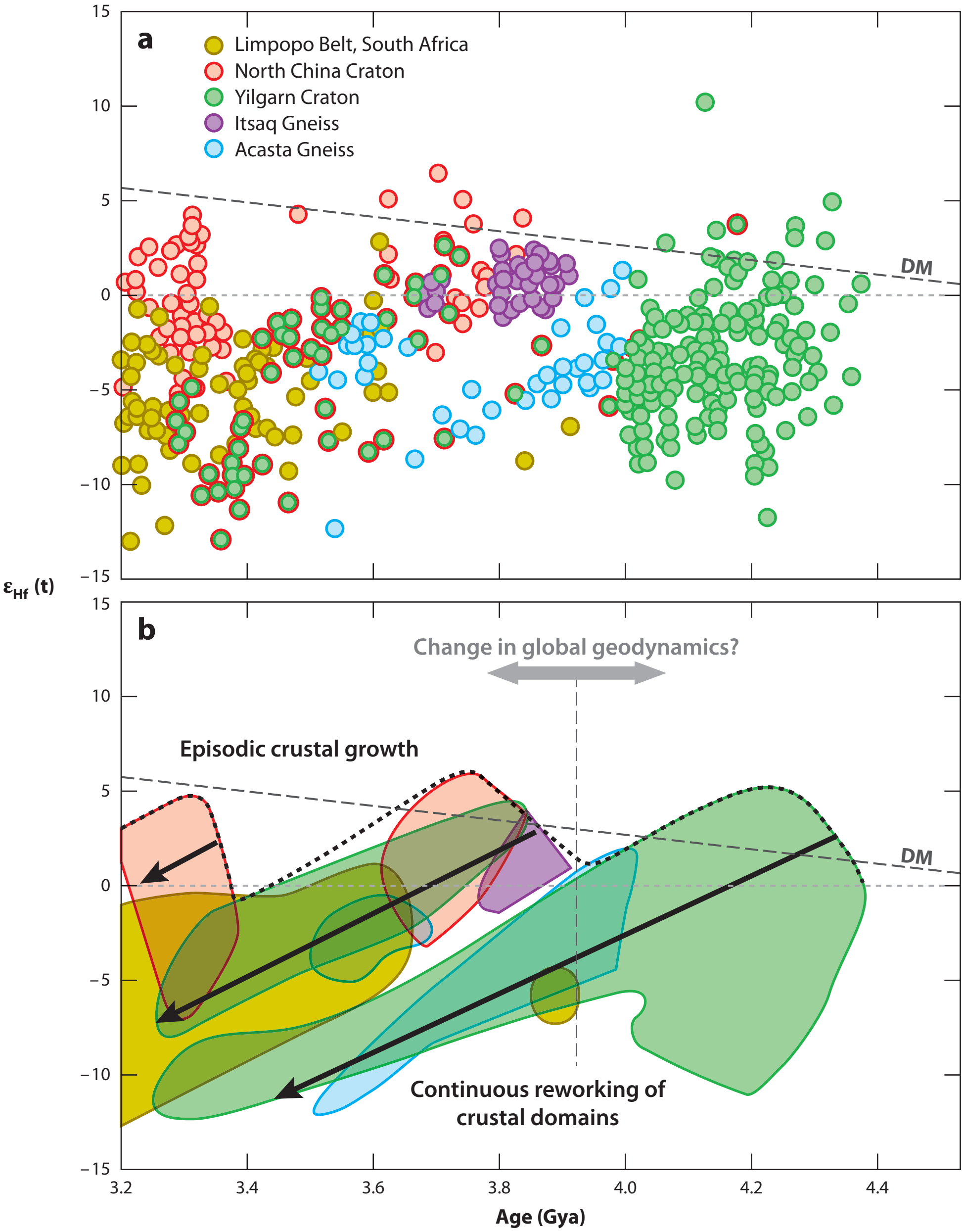

Figure 3

Diagrams showing the Hf isotopic compositions of zircons recovered from the oldest parts of the world. The oldest zircons, from Jack Hills sediments and from Acasta Gneiss, plot largely below the bulk earth composition, indicating that they crystallized in granites that were produced by repeated remelting of a very old enriched source. Only after about 3.9 Gya do zircons with positive ε_{Hf} appear, indicating renewed input from the mantle and perhaps a change in tectonic style. Abbreviation: DM, depleted mantle. The thick black dotted line in panel *b* indicates the upper bound of the data; the black lines with arrows show the effect of reworking of an enriched source of constant composition. Diagrams from Nebel-Jacobsen et al. (2010).

The situation can be compared with that on Mars and Venus. The reappearance of zircons from juvenile granites from approximately 3.9 Gya (**Figure 3**) suggests that the stagnant lid was destroyed at the end of the Hadean, perhaps during the late heavy bombardment. From then on, the intrusion of abundant granites, such as those in the oldest parts of Greenland, Canada, and Australia, signaled the onset of plate tectonics.

THE FAINT YOUNG SUN PARADOX

In 1972, Sagan & Chyba (1997) and Sagan & Mullen (1972) proposed "the faint early sun paradox." The life history of a small yellow star like our Sun is well known from astronomical observations: After an early hyperactive infancy (the T-Tauri stage of intense and variable X-ray and radio emissions), the sun started a warming sequence that continues to the present. Four billion years ago, its luminescence was approximately 30% less than it is now. Given that the modern Earth is prone to glaciation under a much warmer Sun, it might be expected that the faint young Sun illuminated an Archean planetary surface covered by thick permanent ice. Yet geological observations—the presence at Isua and Nuvvuagittuq of sedimentary rocks that formed 3.8 Gya through fluvial erosion and, crucially, the record in Jack Hills zircons of liquid water, 4.3 Gya—tell us that temperatures at the surface were buffered between 0°C and 100°C for almost all of Earth's history (Sagan & Chyba 1997).

To resolve the paradox, Kasting (1993) suggested that high concentrations of atmospheric greenhouse gases, either CO_2 or perhaps methane, prevented the oceans from freezing over (**Figure 4**). In contrast, Rosing et al. (2010) have argued that the prevalence of magnetite (iron oxide) in Archean sediments and paleosols and the absence of siderite (iron carbonate) indicate that CO_2 levels in the Archean atmosphere were little greater than those of today (**Figure 4**). They suggested that the albedo of the early Earth was lower because of a lack of biologically induced cloud condensation nuclei and because the surface area of continental crust was less. This proposal may be tenable if the continuous-growth model for the formation of continental crust is correct or if oceans were deeper resulting in less exposed land (**Figure 5**).

THE GEOLOGICAL SETTING OF THE ORIGIN AND EVOLUTION OF LIFE

After the Moon-forming event occurred 4.5 Gya (Halliday 2000, 2001), the ocean/atmosphere system and uppermost few kilometers of crust cooled within a few million years. Surface cooling after accretion would then be governed by how quickly CO_2 was removed from the atmosphere by carbonation of the oceanic crust (Sleep et al. 2001, Zahnle et al. 2007). If early subduction were efficient, this could have taken as little as 10 million years, leaving a cold lifeless Earth, its oceans white with ice.

From ~4.4 to 4 Gya, wide areas of the planet may have been covered by lava flows under a deep ice-covered ocean, with widely flooded continental nuclei. The main volatile emitted from volcanic eruptions was water, accompanied by carbon, nitrogen, and sulfur gases. If the core segregated early, as indicated by isotopic data from lead, tungsten, and osmium (e.g., Wood & Halliday 2010), the oxidation state of the lava mantle would have been close to that of the modern mantle (Canil 1997) and the high pressure of submarine degassing resulted in the emission of mainly reduced species such as H_2S and CO_2 rather than SO_2 and H_2O (Gaillard et al. 2011). It is also likely that N_2 was degassed (Kasting et al. 1993.

We favor Armstrong's (1981) model and suppose that the continents were approximately as voluminous then as they are now. The oceanic lithosphere subducted (we see no other credible way of producing the enormous volumes of granite that make up the bulk of Archean continental crust).

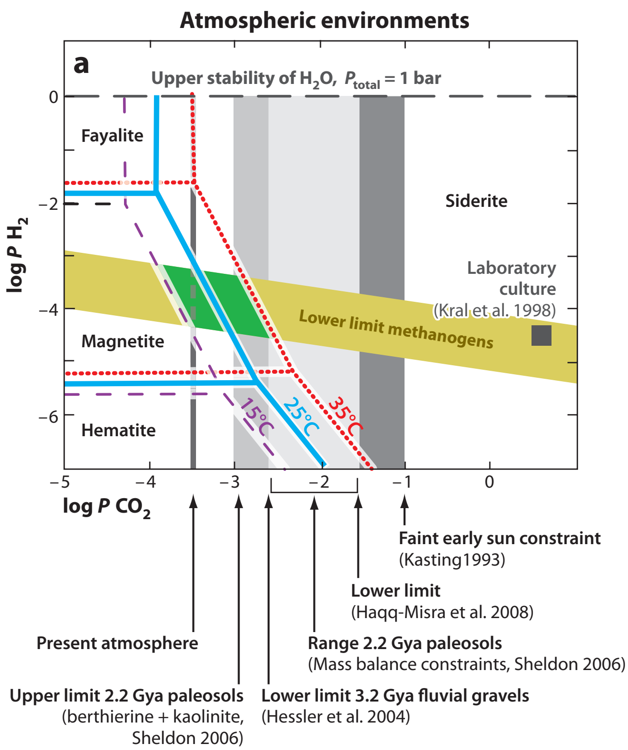

Figure 4

Constraints on the partial pressures for CO_2 and H_2 in (*a*) atmospheric and (*b*) aquatic environments of the early Earth provided by the stability of minerals in the system $FeO–Fe_2O_3–SiO_2–CO_2–H_2O$. From Rosing et al. (2010).

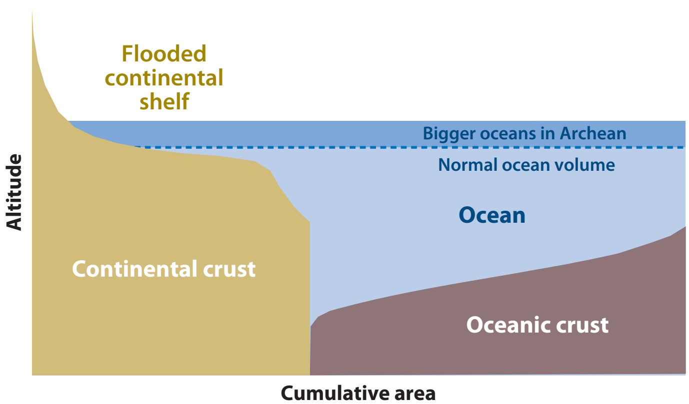

Figure 5

Schematic diagram illustrating the factors that influence the area of emerged continents and particularly the effect of greater ocean volume. Modified from Flament et al. (2008).

Because of greater radioactive heating, the Hadean-Archean continental crust would have been hotter and, therefore, more ductile and weaker than modern continents. Lofty mountain ranges presumably were absent. Normal oceanic crust may have been almost as thick as continental crust, with high-standing mid-ocean ridges and oceanic plateaus occupying large parts of the ocean basins. In addition, the ocean volume was greater than it is today. As a result, most of the continents, except for the modest mountain ranges, were flooded. Dry land was rare, and where present, it was free of vegetation, although perhaps it contained microbial life where it was wet from rainfall. Exposed rocks, both granite and basalt, may have been subject to rapid alteration from the aggressive CO_2-rich atmosphere, though the effect may have been mitigated by low temperatures beneath the faint young sun.

Circulation of seawater through hot komatiitic and basaltic lavas making up the oceanic crust would have created a variety of hydrothermal chemistries. Close to mid-ocean ridge axes, probably in deep water, the systems emitted hot highly acid fluids, resembling modern black smokers. Farther from volcanic centers, cooler water-rock interaction produced high-pH fluids. In shallower water, as was the case in greenstone belts such as Belingwe, cooling komatiite on the continental crust would have hosted cool, highly alkaline hydrothermal systems. The composition of seawater would have been dominated by input from oceanic hydrothermal systems. Shallow or subaerial hydrothermal systems of major volcanic islands and their erosion would have also affected these systems.

Subduction would have provided andesitic lavas, which likely hosted hydrothermal systems with specific local settings rich in accessible copper and zinc. In addition, hydrothermal systems at mid-ocean ridges provided accessible nickel and copper, and less zinc in localized settings. In modern submarine hydrothermal systems, sulfide is precipitated by microbial action, reduced from oceanic sulfate, itself an indirect product of oxygenic photosynthesis. In the abiotic Hadean, and perhaps also for much of the anoxic Archean, abundant sulfate would likely have been absent (Canfield 2005).

To summarize, by the late Hadean, say, 500 million years after accretion, the planet probably had many sites where the key biochemical necessities were available. Abundant komatiitic volcanism in the Hadean and early Archean is probable. An especially attractive site was provided by the komatiite hydrothermal systems, operating in cooling ultramafic lavas around a large shield volcano and erupting onto a rifted early continental fragment built of andesitic lavas made by subduction.

REDOX CONTRASTS OF THE SURFACE ENVIRONMENT

Life exploits kinetics to sustain chemical disequilibrium. Modern life acquires this by exploiting photosynthesis, which involves immensely complex biochemistry. Nisbet & Sleep (2001) argued it was likely the first organisms were chemo-autotrophs exploiting local redox contrasts. One possible source of life support is the serpentinization of ultramafic rock (komatiite) in seawater hydrothermal systems, thereby creating large regions where hot olivine was in close contact with seawater. Thus, the abiotic H_2 supply to the ocean/atmosphere system may have been much larger than the relatively small flux occurring today from hydration of olivine basalts. Holland (2009) estimated that the total flux of molecular hydrogen in the Hadean was approximately 10^{12}–10^{13} mol/year.

The second, oxidizing side of the accessible prebiotic redox contrast was supplied in the uppermost atmosphere when hydrogen was lost to space, ejected by ultraviolet radiation and also by the solar wind from the young Sun (Sagan & Chyba 1997), before Earth's magnetic field strengthened as the core formed (Tarduno et al. 2010). Evaporation of water vapor directly from warmer ocean patches would also have contributed to planetary hydrogen loss. With cold or icy oceans, only limited H_2O vapor would have been present in the atmosphere. However, during episodes of meteorite bombardment, the ocean surface may have warmed significantly, providing transient episodes when water vapor reached high into the upper atmosphere to have been photolysed and to have the hydrogen ejected, leaving OH and creating oxidation power.

ATMOSPHERIC BUDGETS

There is no direct information about the composition of the end-Hadean atmosphere. The reduced iron-rich core segregated before or immediately after the Moon-forming impact (Halliday 2003), leaving a relatively oxidized mantle. Loss of hydrogen to space meant that atmospheric carbon gases were relatively oxidized and CO_2 was dominant. If the surface temperature in the Hadean were very low under the faint young Sun, there may have been albedo-driven episodes when a CO_2-dominated atmosphere could have collapsed as frozen dry ice. However, given high temperatures around active volcanic centers, the oceans would always have sustained at least a lower zone of liquid water, possibly under thick ice cover. Ash and dust from huge volcanic eruptions would affect ice albedo, giving warm events.

Little is known about the N_2 content of the air. Planetary accretion endowed the planet with nitrogen compounds such as NH_3 and amino acids that then equilibrated with the mantle. Volcanoes degassed copious N_2 (Yokochi et al. 2009), which is relatively inert and thus would have reacted with few species and had a long residence time in the atmosphere. A variety of volcanic sulfuric gases would also have been emitted, eventually to enter the ocean as soluble oxides or as sulfur droplets. Holland (2009) noted that, in addition to reacting with H_2 in the atmosphere, volcanic SO_2 would have been taken up in gypsum formation, resupplying more H_2 to the ocean/rock interface:

$$CaO + SO_2 + H_2O \rightarrow CaSO_4 + H_2.$$

To summarize, the late Hadean and earliest Archean atmosphere remains opaque to science. Most likely, under the faint young Sun, the air contained N_2, significant CO_2, and minor sulfur and nitrogen gases. Evaporation of the ocean surface supplied the other major greenhouse gas, i.e., water vapor, only if the surface temperature at the equator were significantly above 0°C.

ORIGIN OF LIFE

Although modeling the origins of life may be best left to Nobel-prize-winning biochemists and aspirants, geologists can fill in the background by providing some useful constraints (e.g., Lane et al. 2010, Martin et al. 2008, Sleep 2010). Until recently, it was thought that the time before the late-heavy bombardment from ~3.9 Gya was inclement for life, and that even if life had begun in the Hadean, the bombardment would have sterilized the oceans. However, using thermal modeling, Sleep (2010) considers that by roughly 4.37 Gya some "Goldilocks" regions existed in the oceanic crust where conditions were such that even a major ocean-heating event would not have destroyed newly emerged life. The latest date by which life must have started is set by the strong evidence in the Isua Belt in Greenland dating from ~3.8 Gya (Grassineau et al. 2006, Rosing 1999). S-based metabolisms and, perhaps, anoxygenic photosynthesis may have preexisted and survived any late bombardment.

Among the many suggestions describing the environment in which life began, the most geologically interesting is the hydrothermal variant on Darwin's warm little pond. Lane et al. (2010)

and Martin et al. (2008) focused on alkaline hydrothermal vents, influenced especially by the off-axis "Lost City" system. In such off-axis vents, hydrothermal fluids can be strongly alkaline (pH 9–11) and rich in hydrogen produced by the serpentinization of olivine. The importance of alkaline hydrothermal systems in the emergence of life was noted by Russell et al. (1993), long prior to the discovery of the Lost City system. In the Hadean, with abundant komatiites, such hydrogen-rich alkaline vents may have been common. The resulting volcanic setting could have been in moderately deep water on the flanks of a high-standing mid-ocean ridge, or—perhaps even more attractive as a setting—in shallow waters on the side of a large komatiitic volcano.

INTERPRETING ANCIENT PROTEINS WITHIN THE PRISM OF GEOCHEMISTRY

Many ancient key proteins, especially metal proteins, may have descended from the last universal common ancestor (LUCA). Early life probably had not evolved sophisticated metal-gathering apparatuses, so the metal proteins may have evolved in geochemical settings where the necessary metals were so abundant that they were obtrusive to biological cells. For example, some key pigments vital in extant modern organisms (e.g., $Fe\text{-}N_4$ in heme, $Mg\text{-}N_4$ in chlorophyll) have a central metal surrounded by four nitrogen atoms. Such structures could have formed in high-pH settings—for example, in a hydrothermal system around a cooling komatiite flow. Supply of magnesium and iron from hydrothermal sources would have been crucial to facilitate biochemical reactions in early life. Heat-shock proteins are also common to all life. These include a variety of proteins such as molecular chaperones that repair damage to enzymes and facilitate the folding, unfolding, and assembly of other proteins.

Lane et al. (2010) noted how chemiosmosis may have been the core early bioenergetic process, specifically in the setting of alkaline hydrothermal vents. This makes excellent geological sense. Mulkidjanian (2009) has suggested that pumping out ambient Na^+, which would have been an important task in an alkaline setting, was the original task of ATPase. Later, the system may have been reversed to manage protons, which are harder than Na^+ to bar with biological membranes.

THE EARLIEST RECORDED BIOLOGICAL COMMUNITY: ISUA

The outcrop and geological diversity of the larger fragments of the older geological record have been summarized by Nisbet (1987). The Isua Belt, dating from 3.8 to 3.6 Gya, preserves a wide range of sedimentary and volcanic rocks, in which both isotopic and macroscopic traces of life can be recognized. Rosing (1999) reported carbon dust that is highly fractionated and isotopically depleted in ^{13}C. Given the abundance of the carbon and its dissemination in the sedimentological facies, it is improbable that this dust was abiotic solar system carbon that was isotopically fractionated in space before falling to Earth. It is much more likely that biological processes including carbon fixation or methane production and consumption produced the fractionation now recorded in debris from dead plankton. In other Isua rocks, sulfur isotopes (Grassineau et al. 2006) also suggest biological activity. Although the evidence is not conclusive, microbial sulfate reduction may date from this time.

Methanogenesis, which leaves a record of highly fractionated carbon isotopes, may also be very old. There is no specific support for or against the presence of photosynthetic organisms in Isua times. Non-photosynthetic chemo-autotrophs may have sustained the microbial community, with recycling of dead organic material by heterotrophy. Biological methane, a powerful greenhouse gas, could have warmed the surface. However, an atmosphere rich in methane produces smog clouds, thereby reflecting sunlight. Carbonyl sulfide (OCS), which is an important greenhouse warmer, may also have contributed to greenhouse warming (Ueno et al. 2009).

Isua contains sediments—liquid water was present and erosion was occurring. Rosing et al. (2010) showed that the ubiquitous presence of mixed-valence Fe(II-III) oxides in Archean sediments is difficult to reconcile with high concentrations of greenhouse gases in the Archean air. However, if methanogens had already evolved, biological methane could have been a significant warmer. Pressure broadening of the greenhouse warming by a high atmospheric N_2 concentration may also have contributed to keeping the planet warm, but this also increased Rayleigh scattering of incoming sunlight, yielding a cooling effect (Halevy et al. 2009). Rosing et al. (2010) provide an alternative explanation of the faint young sun paradox: The albedo of the young planet, with its small land areas and large oceans, may have been lower than it is now, especially if there were few dust particles and biological aerosols to nucleate clouds.

THE MID-ARCHEAN: THE HEYDAY OF ANOXYGENIC PHOTOSYNTHESIS

Strong evidence from the mid-Archean geological record indicates that microbial life was abundant. A wide variety of organo-sedimentary rocks has been described from the Pilbara in Western Australia and the Barberton Mountain Land in South Africa. The best evidence for biogenic sedimentary carbonate, including well-preserved, widespread, long-lived stromatolites, comes from the Strelley Pool cherts in the Pilbara, dating from 3.43 Gya (Allwood et al. 2007). These have extensive dolomite/chert stromatolitic laminae and appear to have formed as a reef in a transgressive marine environment, with frequent very saline or evaporitic interludes (Allwood et al. 2006, 2007) and proximal hydrothermal activity. Tice & Lowe (2004) have reported 3,416-million-year-old photosynthetic microbial mats in the Barberton Mountain Land. The Barberton strata preserve evidence for a microbial ecosystem (Westall et al. 2006b) and paleontological evidence for a complex microbial ecosystem (Westall et al. 2006a). Studying the ∼3.3 Gya Josfsdal Chert, Westall et al. (2011) used in situ nanometer-scale techniques to investigate the structural and compositional architecture in a 3.3-Ga-old microbial biofilm, which they concluded was formed by a consortium of anoxygenic microorganisms, including photosynthesizers and sulphur reducing bacteria.

The simplest interpretation of the productivity of these microbial consortia is that they depended on photosynthesis, probably anoxygenic. However, overall, the evidence from the 3.5- to 3.0-Ga-old mid-Archean record suggests anoxic conditions (Farquhar et al. 2007, van Kranendonk et al. 2003). Farquhar & Wing (2003) used the record of mass independent fractionation of ^{33}S to reach the conclusion that there was no oxygen in early to mid-Archean air. This supports the hypothesis, once controversial but now widely held, that anoxygenic photosynthesis came before oxygenic photosynthesis (Nisbet et al. 1995).

LATE ARCHEAN: EVOLUTION OF OXYGENIC PHOTOSYNTHESIS

The history of oxygenic photosynthesis (reviewed by Buick 2008, Canfield 2005, Nisbet et al. 2007) remains extremely controversial. Whereas many authors have suggested it began in the mid- or late Archean, Kopp et al. (2005) considered that oxygenesis began only in the Paleoproterozoic, the time from which the first oxic sediments are found. Although cyanobacteria may have appeared in the Archean, Rasmussen et al. (2008), considered it was more likely that they evolved between 2.45 and 2.32 Gya and that oxidation of ferrous iron by anoxygenic phototrophic bacteria caused deposition of banded iron formation.

Possible insight into the start of oxygenic photosynthesis may come from studies of the drawdown of CO_2 in the air, resulting from a sharp increase in the productivity of the biosphere (which would then rapidly generate methane from decaying organic matter). Preserved primary calcite of unambiguous sedimentary origin is virtually absent from the record prior to 2.9 Gya, though some rocks may have originally been calcitic, but with the carbonate later replaced by silicification. This leads to the hypothesis that the atmosphere before 2.9 Gya was too rich in CO_2 to permit calcite precipitation in the relatively acid seas. Furthermore, sedimentary limestone deposition may only have been possible if a local source of alkalinity were significant (e.g., in a lake or lagoon). Carbonate may then have been replaced in diagenesis as facies shifted and pore waters changed.

The oldest large-scale reef deposits that are still carbonate appeared 2.9–2.8 Gya, in the Pongola Belt in South Africa (Eglinton et al. 2003), at Mushandike in Zimbabwe (Abell et al. 1985), and at Steep Rock in Canada, where the reef is many kilometers long and up to 500 m thick (Wilks & Nisbet 1985). Unlike the earlier mid-Archean examples, which have mainly been silicified, rocks dating from 2.9 to 2.8 Gya are carbonates, both dolomite and limestones. The rocks were laid down in shallow marine settings, and the presence of abundant carbonate suggests the water was not markedly acid. There is no sign of extreme alkalinity, implying that the CO_2 level in the air was modest, in the hundreds to low thousands of parts per million rather than at percentage levels.

Carbon isotopes in most limestones dating from 2.9 Gya ($\delta^{13}C_{carb}$ 0‰) and organic matter ($\delta^{13}C_{carb}$ ∼−25 to −30‰) are remarkably close to modern parallels (Schidlowski & Aharon 1992), implying that carbon dioxide was captured from the atmosphere by cyanobacteria using the enzyme Rubisco I. Nisbet et al. (2007) presented this as strong evidence for oxygenic photosynthesis. There are also signs of glaciation in rocks dating from 2.9 Gya in Southern Africa (Young et al. 1998): Could this have been induced by a sudden drawdown of CO_2 at the onset of oxygenesis?

From approximately 2.7–2.6 Gya, sedimentary carbonates become abundant. Both in Australia and Africa, stromatolites are superbly preserved (Buick 1992, Nisbet et al. 2007). In the Belingwe Belt in Zimbabwe (Bickle & Nisbet 1993), the Manjeri Formation from 2.7 Gya includes small-scale limestone reefs, and its sedimentary facies vary from oxic shallow-water environments through mixed subtidal facies with both oxic and anoxic facies to strongly anoxic deepwater facies well below the wave base. Evidence from sediment facies, carbon and sulfur isotopes (Grassineau et al. 2002), and iron isotopes (Archer & Vance 2006) supports this conclusion. The Manjeri Formation is overlain by a thick sequence of komatiitic and mafic lavas and above them lies the dominantly shallow-water ∼2.65-Ga-old Cheshire Formation, which includes luxuriant stromatolite reefs in very shallow-water and evaporitic lagoons. Textural and isotopic evidence—$\Delta^{34}S$ (Grassineau et al. 2002), $\Delta^{33}S$ (C. Thomazo, N.V. Grassineau, H. Strauss, M. Peters, E.G. Nisbet, manuscript in preparation) and molybdenum (Siebert et al. 2005)—imply that the shallow water was locally oxic, not anoxic. As with the 2.9-Ga-old successions, $\delta^{13}C_{carbonate}$ values have a modern-looking aspect. In the Cheshire carbonates, $\delta^{13}C_{carbonate}$ clusters around $+0.2 \pm 0.3$‰, whereas $\delta^{13}C_{organic\ matter}$ is -28.6 ± 3.3‰ (Nisbet et al. 2007). The simplest inference is that organic carbon in the Belingwe rocks was captured from the globally mixed ocean/atmosphere system by oxygenic photosynthesis (Nisbet et al. 2007).

The Australian record leads to similar inferences (Buick 1992). From a wide variety of multiproxy studies, Anbar et al. (2007) showed evidence that there was a "whiff of oxygen" in the Late Archean. Czaja et al. (2010) found wide excursions in $\delta^{13}C$ and bulk/mineral $\delta^{56}Fe$ values in rocks 2.5–2.7 Ga old, which they interpreted as evidence for C cycling by various anaerobic or aerobic methane pathways. They interpreted Fe isotopes in shallow-water carbonates as evidence for Rayleigh fractionation during $Fe^{2+}{}_{aq}$ oxidation by O_2 in the water column. Much isotopic evidence—including $\Delta^{33}S$; molybdenum, iron, rhenium, and uranium (Duan et al. 2010, Kendall et al. 2010, Raiswell et al. 2011); as well as rare earth element (REE) study (Kerrich & Said 2010)—

suggests mild environmental oxygenation in coastal waters from 2.7–2.5 Gya. Nevertheless, there is also strong evidence for anoxia (Rasmussen et al. 2008). It is likely that the Late Archean waters were typically subject to shallow-to-deep redox stratification, with transient upwellings and downwellings and local shallow-water oxygen "oases" in the photic zone. However, Guilbaud et al. (2011) note that Archean iron-isotope excursions do not necessarily record dissimilatory Fe(III) reduction or particular redox conditions. Moreover, Sim et al. (2011) queried whether there is sulfur-isotope evidence for an oxidative sulfur cycle.

Large-scale volcanic eruptions inject various sulfur species into the high atmosphere, where ultraviolet photolysis produces mass-independent fractionation (MIF) of sulfur isotopes. Such fractionation occurs on the modern Earth—for example, in Antarctic snow under the polar vortex that downwells from the stratosphere (Baroni et al. 2007), with a changing sign of $\Delta^{33}S$ over time from an initial positive component to a negative value. However, even with only modest amounts of O_2 in the air, sulfur will be rehomogenized before preservation in sediment, and the chance of preserving the MIF in sediment is very low (Savarino et al. 2003). The Archean MIF record shows a threefold pattern: (*a*) moderate early Archean MIF anomalies with $\Delta^{33}S < 4‰$, (*b*) small anomalies ($<1‰$) 3.4–2.6 Gya, (*c*) then large signals (up to 12‰) at the very end of the Archean. This is most simply interpreted as a broad record of anoxic conditions, but the detail is extremely controversial. For example, the MIF evidence led Halevy et al. (2010) to conclude bacterial sulfate reduction was unimportant prior to 2.5 Gya, an inference consistent with the mid-Archean findings of Philippot et al. (2007) but difficult to collate with the ~35‰ range in $\delta^{34}S$ from −18‰ to +17‰ seen in Belingwe (Grassineau et al. 2002), or with molecular phylogeny.

Halevy et al. (2010) interpreted the spike in MIF in the latest Archean (2.7–2.5 Gya) as a consequence of an elevated volcanic SO_2:H_2S ratio, which they attributed to a major shift in volcanic style from submarine to subaerial eruption. As revealed by our very fragmentary record, major changes occurred in global volcanism around this time. Hayes (1994) suggested that an episode of global methanotrophy occurred at the Archaean-Proterozoic transition, but this may have been followed by a reduction in methane emission and then a buildup of oxygen in the global atmosphere. To explain this, Konhauser et al. (2008) pointed to the marked decline in komatiite eruption after approximately 2.7 Gya and suggested a nickel famine occurred as a result. Nickel is a key metal cofactor in several enzymes of methanogens, and they proposed that its decline would have stifled methanogen activity in the ancient oceans and disrupted the supply of biogenic methane.

Figure 6 is a synopsis of the possible redox evolution of the ocean-atmosphere system. Nisbet et al. (2011) have made the controversial proposal that the action of natural selection on the enzyme rubisco has been the basic kinetic regulator of the atmospheric CO_2:O_2 ratio and hence the greenhouse.

THE NITROGEN AND PHOSPHATE PROBLEMS

Today, the atmospheric reservoir and atmospheric lifetime of N_2 are set by the balance (Canfield et al. 2010) between, on the one hand, processes fixing nitrogen, including both biological nitrification and lightning fixation, and, on the other hand, formation of N_2 by denitrification and by planctomycete bacteria that make N_2 by combining NH_4^+ and NO_3^- in the anammox process. It is likely that N_2 was present in the late Archean air. Lightning may have abiotically converted some N_2 to compounds that then dissolved in water. In hydrothermal systems, these dissolved compounds would interact with reducing fluids and precipitate as ammonium zeolites in seabed metamorphic assemblages to enter the mantle via subduction. Thus, the N_2 content of the air, and the nitrogen budget of the surface environment, would have depended on the

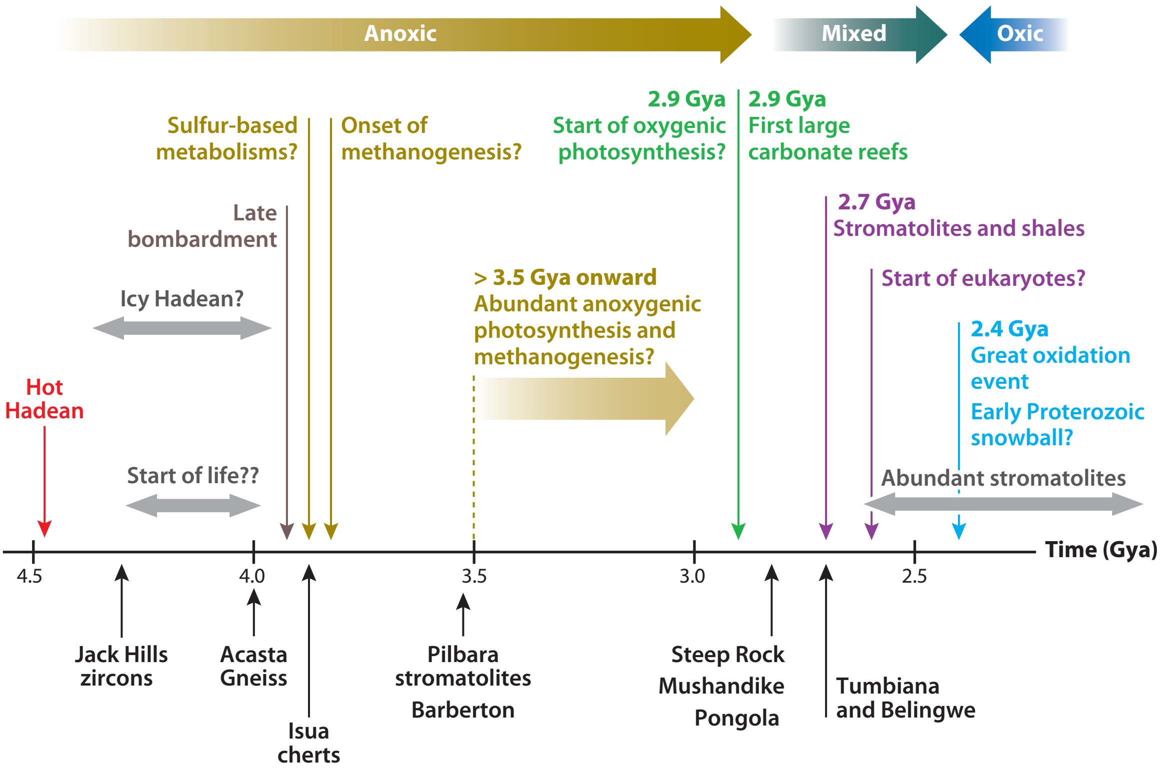

Figure 6

Changes in the composition of the atmosphere through time. Modified from Nisbet & Fowler (2011).

relative rates of volcanic degassing, the mix of degassed nitrogen species, and the rate of nitrogen fixing. Significant soluble nitrogen must have been accessible to life, presumably from volcanic nitrogen gases and from fixed N_2. Vlaeminck et al. (2011) reviewed the suggestion that microbial nitrogen oxidation began with methanotrophic bacteria, with a primordial role among ammonia oxidizing archea, whereas the descent of early nitrate production may have been via anammox planctomycetes, followed by Nitrospira. Biological intervention in the nitrogen cycle may be of great antiquity, and the anammox reaction and planctomycete formation of N_2 may also be very old (Yang et al. 2005).

The central change that permitted a closed-nitrogen cycle coincided with the evolution of the nitrogen-fixing enzyme nitrogenase (Falkowski et al. 2008). Nitrogenase is an FeMo enzyme, now widely distributed across many phyla but which very probably evolved from a single source. Nitrogenase demands strictly anaerobic conditions to operate, suggesting that it evolved as an iron enzyme in an anaerobic ocean lacking soluble molybdenum. Despite the sensitivity of nitrogenase to oxygen poisoning, at some stage, some cyanobacteria took the remarkable step of colocating nitrogen-fixing heterocysts with oxygenic photosynthesis. This may have occurred in a setting where alternating oxic and anoxic waters met (e.g., in a coastal lagoon subject to inflows of anoxic oceanic waters from below the photic zone).

In contrast to carbon isotopes, which are preserved both in carbonate minerals and in organic matter that constitute a significant proportion of the rock, the protection of nitrogen against later alteration is more hazardous. The oldest (3.8–3.2 Gya) nitrogen-isotopic signatures in Archean rocks have $\delta^{15}N$ values from -7 to $+7‰$, whereas younger (3.2–2.5 Gya) Archean organic matter is more ^{15}N enriched, with $\delta^{15}N$ approximately $+11‰$ (Thomazo et al. 2009). Abundant biogenic kerogens in 2.7-Ga-old cherts and banded ironstones show enrichment in ^{15}N (with $\delta^{15}N$ from $+24‰$ to $+35‰$). Thomazo et al. (2009) suggested that $\delta^{15}N$ decreased to the modern average value of $+5‰$ when oceanic nitrate content increased after oxygenation of the ocean at the end of the Archean. However, they cautioned that original pristine metabolic signatures in $\delta^{15}N$ may be influenced by postdepositional changes such as thermal metamorphism and alteration.

Understanding how life gained access to a biologically useful supply of phosphorus remains a key puzzle. Early Hadean carbonate subduction may have permitted the eruption of carbonatite that could have supplied phosphate, but this rock type lies at the opposite end of the magmatic spectrum from komatiite and should have been rare or absent in magmas produced in the hot Archean mantle. From a study of phosphorus to iron ratios in Archean iron formations, Planavsky et al. (2010) considered that dissolved silica concentrations in the Archean ocean may have been as low as the cristobalite saturation level (0.67 m*M*) but were more likely to have been near amorphous silica saturation (2.2 m*M*). Phosphate concentrations in Earth's early oceans may have been several times higher than Phanerozoic levels. Perhaps the answer to the phosphate problem lies in the composition and physical conditions in the Archean ocean and its ability to retain or precipitate high concentrations of phosphate and other compounds. Holm et al. (2006) suggested, for example, that secondary magnesium hydroxide (brucite) scavenges borate and phosphate from seawater. Deposition of this mineral around alkaline hydrothermal vents may concentrate phosphorus in sites also rich in nickel, copper, and other essential metals.

EVOLUTION OF EUKARYOTES

There is much dispute about the early history of the eukaryotes. Javaux et al. (2010) suggested that large microfossils in 3.2-Ga-old estuarine sediments may have been eukaryotic, but the evidence, though interesting, is not definitive (Buick 2010).

Evidence from molecular fossils supports the inference of great microbial diversity and the existence of aerobic habitats in Late Archean time. Waldbauer et al. (2009), studying bitumens dating from 2.67 to 2.46 Gya, found evidence of hopanes attributable to bacteria, and steranes of eukaryotic origin. They concluded that the molecular fossil record supports an origin in the Archean Eon of the three Domains of cellular life, as well as of oxygenic photosynthesis and the anabolic use of O_2.

All protists carry organelles related to mitochondria (e.g., mitosomes, hydrogenosomes, etc.) and possess genes of α-proteobacterial descent (Embley & Martin 2006). From a molecular-clock study of protein folds, Wang et al. (2011) suggested that aerobic metabolism emerged approximately 2.9 Gya and that oxygen then triggered a major diversification of life. This broadly tallies with the isotopic evidence.

Hampl et al. (2009) used protein phylogenomic analysis of 48 taxa to identify three primary divisions within eukaryotes. The monophyletic suprakingdom-level group comprises the Excavata; the unikonts; and a megagroup of Archaeplastida, Rhizaria, and the chromalveolate lineages. In reviewing the competing hypotheses of eukaryote phylogeny, Rogozin et al. (2009) identified three competing topologies: (*a*) a Crown group topology, in which plants and animals form one line, distinct from other early-branching protests; (*b*) a two-way initial split between unikonts (metazoa, fungi, etc.) and bikonts (plants, algae, Excavata); and (*c*) a "big-bang" split in which all five supergroups of eukaryotes diverged immediately from a common origin. Using genome-wide analysis of rare genetic changes, Rogozin et al. (2009) favored a scenario in which the first split

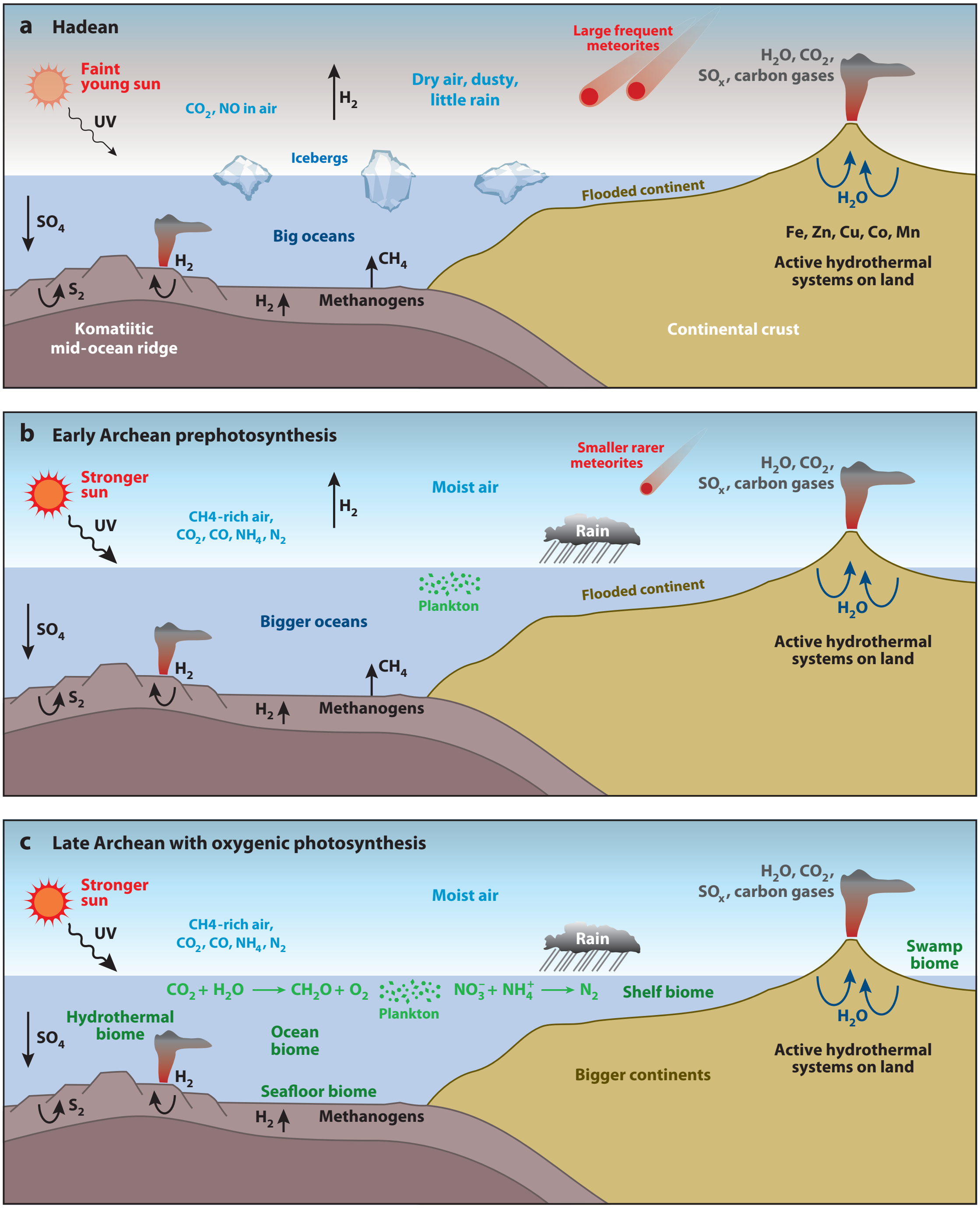

Figure 7

Model of the evolution of the planetary surface: (*a*) the Hadean surface, possibly glacial (apart from rare very hot events after major meteorite impacts); (*b*) the early Archean surface, before the onset of photosynthetic processing of the air; and (*c*) the late Archean surface, assuming that the major biochemical pathways had evolved and that the main groups of prokaryotes had evolved. Modified from Nisbet & Fowler (2004).

in eukaryote evolution took place between photosynthetic and nonphotosynthetic forms, perhaps triggered by endosymbiosis between an ancestral unicellular eukaryote and a cyanobacterial parent of chloroplasts.

CONCLUSION

The past decade has brought much geological insight into the puzzles of the Hadean and Archean, and some model-building (**Figure 7**). Isotopic study of the evolution of the crust and mantle, as recorded in igneous and metamorphic rocks, has radically changed our view of the early Earth. Similarly, field discoveries and geochemical research into the record of life in Archean sediments have much improved our understanding of microbial evolution and how life changed the air and reshaped the environment. Looking forward, it is likely that significant advances in the next decade will come from the interaction of molecular biochemistry with geochemistry, especially if new field discoveries are made, for example, through drilling. The surface has barely been scratched. We may never be sure how life began, but we can say much about the setting in which it evolved and prospered.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

We are grateful for insight and helpful criticism during the review process. Archean fieldwork is a cooperative work, and we thank the very many people who have worked with us in the field and lab, as coauthors or associates. In particular, we thank Catherine Chauvel, C. Mary R. Fowler, and Mike Bickle.

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Annual Review of Earth and Planetary Sciences

Volume 40, 2012

Contents

Indexes

Errata

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