Space Sci Rev (2007) 129: 35–78
DOI 10.1007/s11214-007-9225-z

Emergence of a Habitable Planet

**Kevin Zahnle · Nick Arndt · Charles Cockell ·
Alex Halliday · Euan Nisbet · Franck Selsis ·
Norman H. Sleep**

Received: 16 March 2006 / Accepted: 17 January 2007 / Published online: 25 July 2007

Abstract We address the first several hundred million years of Earth's history. The Moon-forming impact left Earth enveloped in a hot silicate atmosphere that cooled and condensed over ~1,000 yrs. As it cooled the Earth degassed its volatiles into the atmosphere. It took another ~2 Myrs for the magma ocean to freeze at the surface. The cooling rate was determined by atmospheric thermal blanketing. Tidal heating by the new Moon was a major energy source to the magma ocean. After the mantle solidified geothermal heat became climatologically insignificant, which allowed the steam atmosphere to condense, and left behind a ~100 bar, ~500 K CO_2 atmosphere. Thereafter cooling was governed by how quickly CO_2 was removed from the atmosphere. If subduction were efficient this could have

K. Zahnle (✉)
NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035, USA
e-mail: Kevin.J.Zahnle@nasa.gov

N. Arndt
LGCA, University Joseph Fourier, 1381 rue de la Piscine, 38401 Grenoble, France

C. Cockell
Planetary and Space Sciences Research Institute, Open University, Milton Keynes, MK7 6AA, UK

A. Halliday
Department of Earth Sciences, University of Oxford, Oxford, OX1 3PR, UK

E. Nisbet
Department of Geology, Royal Holloway, University of London, Egham, Surrey, TW20 0EX, UK

F. Selsis
Ecole Normale Supérieure de Lyon, Centre de Recherche Astronomique de Lyon, 46 Allée d'Italie, 69364 Lyon, Cedex 07, France

F. Selsis
CNRS UMR 5574, Université de Lyon 1, Lyon, France

N.H. Sleep
Department of Geophysics, Stanford University, Stanford, CA 94305, USA

taken as little as 10 million years. In this case the faint young Sun suggests that a lifeless Earth should have been cold and its oceans white with ice. But if carbonate subduction were inefficient the CO_2 would have mostly stayed in the atmosphere, which would have kept the surface near $\sim$500 K for many tens of millions of years. Hydrous minerals are harder to subduct than carbonates and there is a good chance that the Hadean mantle was dry. Hadean heat flow was locally high enough to ensure that any ice cover would have been thin (<5 m) in places. Moreover hundreds or thousands of asteroid impacts would have been big enough to melt the ice triggering brief impact summers. We suggest that plate tectonics as it works now was inadequate to handle typical Hadean heat flows of 0.2–0.5 W/m^2. In its place we hypothesize a convecting mantle capped by a $\sim$100 km deep basaltic mush that was relatively permeable to heat flow. Recycling and distillation of hydrous basalts produced granitic rocks very early, which is consistent with preserved >4 Ga detrital zircons. If carbonates in oceanic crust subducted as quickly as they formed, Earth could have been habitable as early as 10–20 Myrs after the Moon-forming impact.

Keywords Hadean Earth · Moon-forming impact · Origin of Earth · Magma oceans · Planetary atmospheres · Late heavy bombardment

1 Introduction

Percival Lowell, the most influential popularizer of planetary science in America before Sagan, described in lively detail a planetology in which worlds formed hot and dried out as they aged (Lowell 1895, 1906, 1909). Large worlds cooled slowly, and were still evolutionarily young in 1895, "while in the moon we gaze upon the last sad age of decrepitude, a world almost sans air, sans sea, sans life, sans everything." One reason is that gases escape to space. "The maximum speed [a molecule] may attain Clerk–Maxwell deduced from the doctrine of chances to be seven-fold the average. What may happen to one, must eventually happen to all." Another reason presumes cooling. "As the [internal] heat dissipates, the body begins to solidify, starting with the crust. For cosmic purposes it undoubtedly still remains plastic, but cracks of relatively small size are both formed and persist. Into these the surface water seeps. With continued refrigeration the crust thickens, more cracks are opened, and more water given lodgement within, to the impoverishment of the seas." In many respects the modern story, if not the prose, broadly resembles Lowell's.

Lowell's speculations were rooted in Lord Kelvin's concepts of time. Kelvin derived the age of the Earth from the near surface thermal gradient (Kelvin 1895; Schubert et al. 2001; Wood and Halliday 2005). He made the explicit assumption that the Earth cooled by thermal conduction and the implicit assumption that the Earth harbored no unknown energy sources. He obtained an age for the Earth of 25 million years. Kelvin also computed the age of the Sun, in this case by presuming a convecting body for which gravitational contraction was the only energy source, and he obtained a similar age. These are the sort of coincidences that make for a robust theory, or at least a stubborn theorist, and Lowell was one among many to accept these arguments. In the context of Kelvin's history of brief time, monotonically cooling planets made sense: fate was ruled by the surface-to-volume ratio.

The discovery of radioactive heating triggered a relatively brief (and in retrospect ill-considered) counter-reaction in favor of a cold early Earth, in which the only primary source of heating was radioactive decay. In this story the slow internal build up of radiogenic heat eventually led to internal melting after hundreds of millions or even billions of years. A credible consequence of cold formation might be a hydrogen–methane–ammonia primary atmosphere (Urey 1951). Such an atmosphere would be conducive to the abiotic synthesis of complex organic molecules (Miller 1953). Cold formation got a foothold in textbooks, but the enormous gravitational energy released during accretion was never plausibly made to go away. Hot formation eventually returned to favor when it became more fully appreciated that accretion took the form of giant impacts (Safronov 1972; Wetherill 1985).

Of more moment to us here is that Lowell placed the origin of life in a Hadean realm of geothermal heat hidden from the Sun. Perhaps he saw no choice; 25 million years is not necessarily a lot of time. It is now known that the mantle cools by solid state convection, and that the Earth is more than 4.5 billion years old. This leaves plenty of time. Yet the suspicion remains widespread that life arose on Earth in a Hadean realm that is hidden from the rock record (Cloud 1988; Chyba 1993). The Hadean is important because it set the table for all that came later (*ibid*).

1.1 The Hadean Today

Today the Hadean is widely and enduringly pictured as a world of exuberant volcanism, exploding meteors, huge craters, infernal heat, and billowing sulfurous steams; that is, a world of fire and brimstone punctuated with blows to the head. In the background a red Moon looms gigantic in the sky. The popular image has given it a name that celebrates our mythic roots. As Kelvin and Lowell understood, a hot early Earth is an almost inevitable consequence of fast planetary growth. The apparent success of the Moon-forming impact hypothesis (Benz et al. 1986; Hartmann et al. 1986; Stevenson 1987; Canup and Righter 2000; Canup and Asphaug 2001; Canup 2004) has probably evaporated any lingering doubts. Earth as we know it emerged from a fog of silicate vapor.

1.2 Defining the Hadean

Discord confuses what “Hadean” means or should mean (Nisbet 1985, 1991, 1996). One choice has been to define the Hadean as the time before the first rock (currently the Acasta Gneiss, dated to 4.00–4.03 Ga, Bowring and Williams 1999). This puts the Hadean into the same category as the fastest mile or the tallest building. Another choice is to define it as the time before the first evidence of life. This definition was in use at one time. Before Cloud split it into the Hadean and the Archean Eons, there had been a lifeless “Azoic” Eon. “Archean” means “beginning” in the context of life (Nisbet 1982). This definition is consistent with geological convention but is open to endless debate over what constitutes evidence of life. Later, Cloud (1983, 1988) set the origin of life in the Hadean. A potentially useful definition is to synchronize the end of the Hadean with the end of the heavy bombardment of the inner solar system. This would encourage comparisons between planets. On the other hand, the end of the late bombardment is not (yet?) well defined as an instant in time, nor has it shown itself clearly in the terrestrial record. This leaves picking an arbitrary date. Cloud (1983) used 3.8 Ga, others have used 4.0 Ga. All of these definitions are in effect equal at present.

The Hadean record is not data rich. Any tale of the Hadean truly told would be so obscured with qualifications, caveats and prevarications that the reader would need a GPS system just to follow the narrative thread. We have opted instead to present a web of speculations in flat declarative sentences, constrained by basic physics when possible. This is the same point of view taken by Stevenson (1983) in an earlier essay on the topic. That our authoritative-seeming sentences often differ from Stevenson’s authoritative-seeming sentences can be taken as a sign of progress.

2 Astrophysical Context

2.1 The Interstellar Environment

Stars can form in dense clusters in which massive stars live short, brilliant lives, or they can form in quiet low-density suburbs where massive stars are rare. Massive stars dominate their environment. In general massive stars are very hot and extremely luminous and most of their light is emitted in the UV; such a star can emit 10^{10} times more UV than does our Sun. A nearby massive star can be a bigger source of ionizing UV radiation to the solar system than the Sun itself. Interstellar UV can drive photochemistry, and it can also photoevaporate the nebular disk from which the Sun and planets formed (Adams et al. 2004). Stellar UV can also drive off primary atmospheres of small planets. As massive stars hurry toward death they unleash enormous stellar winds that pollute the nebula with fresh products of stellar nucleosynthesis. The biggest stars end as supernovae. Supernovae provide the prime source of short-lived radionuclides such as ^{26}Al and ^{60}Fe. Astronomical observations of γ-rays from ^{26}Al decay imply that the current average ^{26}Al/^{27}Al ratio in the interstellar medium is 9×10^{-6} (Diehl et al. 2006). This is notably lower than the primordial solar system ratio of 5.25×10^{-5} (Bizzarro et al. 2004). The half-life of ^{26}Al is 7×10^5 yrs. The implication is that the solar nebula was enriched with the products of a recent nearby supernova or supernovae. Evidently the Sun did not form in a quiet low-density suburb (Adams and Laughlin 2001). Nearby supernovae could have had other interesting effects on the Sun's environment. But massive stars destined for supernova last only a few million years (Arnett 1996). By the time the Sun reached the main sequence it was well entrenched in its suburban tract home. Any further speculation on these matters is beyond the scope of this essay.

2.2 The Faint Young Sun

According to the standard model, the Sun has steadily brightened since it arrived on the Main Sequence 4.52 billion years ago (the Zero-Age Main Sequence, or "ZAMS"). In the next billion years the Sun brightened from about 71% to 76% of its current luminosity. Standard solar evolution is shown in Fig. 1.

The faint young Sun imposes a stringent constraint on the climate of the young Earth (Ringwood 1961; Sagan and Mullen 1972). Without the addition of potent greenhouse gases the early Earth should have been at most times and places frozen over. This is important and will be discussed in more detail in the following.

The one way to make the young Sun brighter is to make it more massive than it is now. The Sun loses mass through the solar wind. At current rates the mass loss is tiny, amounting to only 0.01% of the Sun's mass over 4.5 Gyrs. To be as bright as it is now, the ZAMS Sun would have needed 6% more mass (Sackmann and Boothroyd 2003). This amount of mass loss far exceeds what is plausible. By studying stellar winds of a half-dozen Sun-like stars, Wood et al. (2002) found that a Sun-like star loses about 0.5% of its mass after it reaches the Main Sequence. This is too small to be important. Wood et al. (2005) have since characterized the winds of another half-dozen solar analogues. According to the newer study the total mass loss from the main sequence Sun was only $\sim$0.1% of its initial mass.

There is little evidence bounding mass loss from very young stars[1]. In 2002 Wood et al. argued that the empirical upper limit on X-ray flux implies a parallel upper limit on mass

[1] When stars are still accreting they generally have extremely large stellar winds, but these typically do not last more than a few million years at most, and given that the stars are accreting, the winds do not imply that the star is on net losing mass.

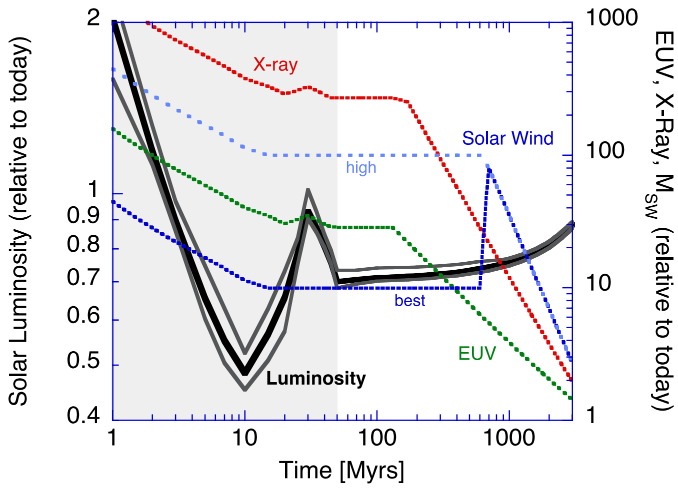

Fig. 1 The first 3 billion years of solar evolution. The solid curves show luminosity evolution. Main sequence luminosity evolution follows Sackmann et al. (1993). Pre-Main Sequence evolution (*shaded region*) is adapted from D'Antona and Mazzitelli (1994). The range of uncertainty is determined by mass loss. Preferred mass loss follows Wood et al. (2002, 2005). Sensitivity to mass loss is scaled from Sackmann and Boothroyd (2003). The upper bound on luminosity arbitrarily multiplies Wood et al.'s best estimate by a factor $4.56t^{-1}$, where t is the age of the Sun in Gyrs. Even with these relatively enormous solar winds the Sun's luminosity is barely affected. The solar wind, X-ray, and EUV evolutions (*broken curves*) follow Wood et al.'s recommendations and references therein. These latter are aspects of solar activity rather than solar luminosity—young stars are generally more active than the sedate modern Sun. The observed scatter in X-ray luminosities of young Sun-like stars (not shown) implies an order of magnitude uncertainty during the Hadean

loss rates; in 2005 they showed evidence that stellar winds may be *smaller* in stars younger than 0.7 Ga than they become later. This is rather surprising. Still, the data offer no support for a markedly more massive young Sun. The range of solar evolutions permitted by Wood et al.'s mass loss rates is shown in Fig. 1.

Often overlooked is that, irrespective of mass loss, the Sun's luminosity was far from constant in the 50 Myrs it took to contract to the main sequence[2]. Figure 1 includes a model of the Sun's pre-main-sequence evolution beginning at 1 Ma (D'Antona and Mazzitelli 1994). During the first few million years the Sun was brighter and redder than it is now. At 10 million years it was only half as bright as it is now, while at 30 million years it was almost precisely as bright as it is now. Thereafter the Sun faded to its ZAMS luminosity as the nuclear fires took over.

These time scales are comparable to the time scales currently seen as relevant to terrestrial planet accretion. Runaway growth of the first generation planets is thought to have taken no more than 1 Myr (Lissauer 1993; Chambers 2004). Planetary embryos, at first embedded in the nebula, would have emerged to see a bright red Sun. Earth and Venus were built by collisions between planetary embryos over some ~50 Myrs. As they grew the planets would have experienced major changes in solar luminosity. These changes were important because they determine the physical state of water in our part of the Solar System. As the Sun changed brightness the water condensation front would have

[2]If this time scale looks familiar, it is: it's Kelvin's time scale for gravitational contraction. This is the part of the Sun's evolution that predates the onset of significant nuclear fusion.

swept back and forth through the solar system. For a planet at Earth's distance from the Sun, at 2 Myr any water present would have been vapor, while at 10 Myr the water would have been ice, and ice would have stable at Venus. It is possible in Mars we are looking at a planet that is old enough to remember these times (Lunine et al. 2003; Halliday and Kleine 2006). In any event, the history of volatiles is sensitive to solar luminosity, and hence the eventual states of Venus and Earth would have been sensitive to the growth spurts of the young Sun.

2.3 The Active Young Sun

In contrast to luminosity in general, the active young Sun was a much stronger source of ultraviolet light, X-rays, and solar wind than it is today (see Fig. 1; see also the chapter by Kulikov et al. 2007, this issue). This inference is based on empirical observations of hundreds of young solar analogs. The theory is not fully developed, but in broad outline stellar activity (sunspots, flares, UV, X-rays, etc.) is directly related to the strength of the magnetic field, which in turn is generated from the star's rotation. As the star ages it loses angular momentum through the stellar wind. Solitary stars are like spinning tops. They all slow down.

3 The Age of the Earth and Solar System

There are no rocks surviving from the first 500 Myrs of Earth's history. The oldest zircon grain found thus far yields an age >150 Myrs after the start of the Solar System (Wilde et al. 2001). Therefore, deducing Earth's earliest history is strongly dependent on geochemistry, theory and comparison with other solar system objects using meteorites and returned samples. The Earth was formed through successive accretion events involving objects as large as other planets. As such the Earth has no simple "age" because it formed from combining earlier formed planetary objects which already had established their own differentiated reservoirs, including cores and atmospheres. We can determine the rate at which the Earth grew by making certain assumptions about the degree of mixing and equilibration between these planets as they coalesced. We can also define the start of the Solar System and this growth history very precisely. Chondrites are the most common form of meteorite landing on Earth. They are thought to represent early dust and debris from the circumstellar disk from which the planets grew. Most chondrites contain refractory Ca–Al-rich inclusions (CAIs) enriched in elements expected to condense at very high temperatures from a hot nebular gas. These are the oldest objects yet identified that formed in the Solar System. CAIs from the Efremovka chondrite have been dated by $^{235/238}$U–$^{207/206}$Pb at 4.5672 ± 0.0006 Ga (Amelin et al. 2002). This is the current best estimate of the start to the Solar System and hence defines a more precise slope to the meteorite isochron (called the "Geochron") first established by Patterson (1956) (Fig. 2). To sort out the growth history of planets it is necessary to use short-lived nuclides, dynamic simulations of planet formation and petrological constraints on likely core formation scenarios.

Short-lived nuclides provide a set of powerful tools for unraveling a precise chronology of the early solar system. The advantage of these is that the changes in daughter isotope can only take place over a restricted early time window; there is no correction for the effects of decay over the past 4.5 billion years. A disadvantage is that the parent isotope can no longer be measured. Hence its abundance at the start of the solar system must first be determined by comparing the isotopic composition of the daughter element in rocks and minerals of independently known age. Only then can it provide useful age constraints.

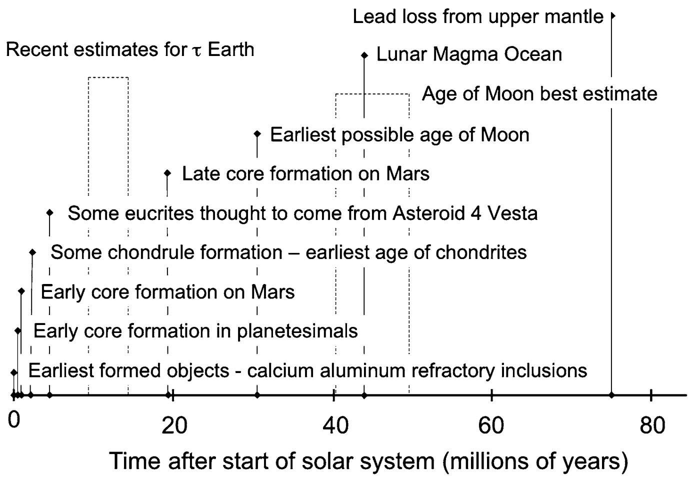

Fig. 2 The current best estimates for the time-scales over which very early inner solar system objects and the terrestrial planets formed. The approximated mean life of accretion (τ) is the time taken to achieve 63% growth at exponentially decreasing rates of growth. The *dashed lines* indicate the mean life for accretion deduced for the Earth based on W and Pb isotopes (Halliday 2003, 2004; Kleine et al. 2002; Yin et al. 2002). The earliest age of the Moon assumes separation from a reservoir with chondritic Hf/W (Kleine et al. 2002; Yin et al. 2002). The best estimates are based on the radiogenic ingrowth deduced for the interior of the Moon (Halliday 2003, 2004; Kleine et al. 2005b). See text for details of other sources. Based on a figure in Halliday and Kleine (2006)

The short-lived nuclides provide most of the information on the first 50 Myrs of the solar system. For example, as well as CAIs, most chondrites also contain chondrules, drop-shaped ultramafic objects with strange textures thought to reflect rapid heating, melting and quenching of pre-existing material in a dusty disk. Using ^{26}Al–^{26}Mg it has been shown that some of these chondrules formed as much as 1 to 3 million years after the start of the Solar System (Russell et al. 1996; Bizzarro et al. 2004) (Fig. 2). Therefore chondrites, the meteorites that contain chondrules, though primitive in composition, must have formed millions of years after the start of the solar system. This is interesting because simulations of planetary accretion indicate that dust should have accumulated into 1000 km-sized planetary embryos in just a few hundred thousand years—much less than the time indicated from chondrule formation. In fact we now have excellent isotopic evidence that a range of accretion styles were involved in the formation of the terrestrial planets. Before discussing this it is worth first explaining the theories behind the formation of Earth-like planets.

3.1 Planetary Accretion

A variety of theories have been advanced for how terrestrial planets form. For a recent review see Chambers (2004). In broad terms the rates of accretion of Earth-like planets will be affected by the amount of mass in the disk itself. If there is nebular gas present at the time of accretion the rates are faster. In fact the absence of nebular gas is also calculated to favor eccentric orbits, which gas would dampen (Agnor and Ward 2002). The presence of solar noble gases in the Earth and Mars is consistent with these requirements. In the simplest terms accretion of terrestrial planets is envisaged as taking place in four stages:

(1) Settling of circumstellar dust to the mid-plane of the disk.
(2) Growth of planetesimals up to $\sim$1 km in size.
(3) Runaway growth of planetary embryos up to $\sim 10^3$ km in size.
(4) Oligarchic growth of larger objects through late-stage collisions.

Stage 1 takes place over time scales of thousands of years and provides a relatively dense plane of material from which the planets can grow. The second stage is the most poorly understood at present but is necessary in order to build objects that are of sufficient mass for gravity to play a major role. Planetesimals would need to be about a kilometer in size in order for the gravitationally driven stage 3 to start.

We do not know how stage 2 happens, although clearly it must. Scientists have succeeded in making fluffy aggregates from dust, but these are all less than a cm in size. How does one make something that is the size of a house or a stadium? One obvious suggestion is that some kind of glue was involved. Volatiles would not condense in the inner solar system. Not only were the pressures too low, but the temperatures were probably high because of heating as material was swept into the Sun (Boss 1990). An alternative is that, within a disk of dust and gas, collective effects can sort or gather particles into pockets of locally high density that might promote collisional coagulation or gravitational collapse (Weidenschilling and Cuzzi 1993; Cuzzi et al. 2005). Local separation and clumping of the material might also lead to larger scale gravitational instabilities, whereby an entire section of the disk has relatively high gravity and accumulates into a zone of concentrated mass (Ward 2000).

However they are formed, runaway growth builds these 1 km-sized objects into 1,000 km-sized objects. The bigger the object the larger it becomes until all of the material available within a given feeding zone or heliocentric distance is incorporated into planetary embryos. This is thought to take place within a few hundred thousand years (Kortenkamp et al. 2000). The ultimate size depends on the amount of material available. Using models for the density of the solar nebula it is possible that Mars-sized objects could originate in this fashion.

Building objects that are the size of the Earth is thought to require a more protracted history of collisions between such planetary embryos. Wetherill (1986) ran Monte Carlo simulations of terrestrial planetary growth and some runs with planets of the right size and distribution to be matches for Mercury, Venus, Earth and Mars. He monitored the time scales involved in these "successful" runs and found that most of the mass was accreted in the first 10 Myrs, but that significant accretion continued for much longer. Wetherill also tracked the provenance of material that built the terrestrial planets and showed that, in contrast to runaway growth, the feeding zone concept was flawed. The planetesimals and planetary embryos that built the Earth came from distances that extended over more than 2 AU. More recent calculations of solar system formation have yielded similar results (Canup and Agnor 2000; Raymond et al. 2004).

Such planetary collisions would have been catastrophic. The energy released is sufficient to raise the temperature of the Earth by thousands of degrees. The most widely held theory for the formation of the Moon is that there was such a catastrophic collision between a Mars-sized planet and the proto-Earth when it was approximately 90% of its current mass. The putative impactor planet, sometimes named "Theia" (the mother of Selene who was the goddess of the Moon), struck the proto-Earth with a glancing blow generating the angular momentum of the Earth–Moon system.

3.2 Tungsten Isotopic Tests for Earth Formation Models

The above models of planet formation differ with respect to timing and can therefore be evaluated using isotope geochemistry. The ^{182}Hf–^{182}W chronometer has been particularly useful in determining the time-scales over which the planets formed. The principle of the technique is that Hf/W ratios are strongly fractionated by core formation because W normally is moderately siderophile whereas Hf is lithophile. Therefore, in the simplest of models, the W isotopic composition of a silicate reservoir such as the Earth's primitive mantle is a function of the timing of core formation. If, however, a planet grows over tens of millions of years, and if as it grows its core gets larger, as is nowadays assumed to be the case for the Earth, the W isotopic composition of the primitive mantle is a function of the rate of growth of the planet.

The silicate Earth has a ^{182}W abundance that is high relative to average solar system. This indicates that some portion of silicate Earth formed as a high Hf/W reservoir during the lifetime of ^{182}Hf. The growth of the Earth must have been protracted, otherwise the ^{182}W abundance would be much larger. How to interpret the results in terms of exact time scales depends on the models used. Because the ^{182}Hf–^{182}W chronometer has a half-life of just 8.9 Myrs, it is insensitive to changes that take place more than 60 Myrs after the start of the solar system. Therefore, the W isotopic composition of the silicate Earth has to be interpreted in terms of a relatively simple growth history of the Earth and its core that takes on board other scientific constraints. The mean life for the Earth assuming an exponentially decreasing rate of growth is 11 Myrs (Yin et al. 2002; Jakobsen 2005). This corresponds to the time taken to achieve 63% growth, which is in excellent agreement with the time scales inferred directly from the simulations of Wetherill (1986).

3.3 Comparisons with Other Objects

Although the Earth accreted over long time scales, the information from studying smaller objects is different. The most recent data for martian meteorites (Kleine et al. 2004; Foley et al. 2005) confirms earlier evidence (Lee and Halliday 1997) that accretion and core formation on Mars were fast. Some recent models (Halliday and Kleine 2006) place the time scale for formation of Mars at less than one million years (Fig. 2). If this is correct, Mars probably formed by a mechanism such as runaway growth, rather than by protracted collision-dominated oligarchic growth. In other words, Mars may represent a unique example of a large primitive planetary embryo with a totally different accretion history from that of the Earth. Lunine et al. (2003) drew a similar conclusion based on the low quantity and high D/H ratio of martian water.

A similar story is being recovered from iron meteorites. With extensive replication and better mass spectrometers very high precision can now be achieved on the W isotopic compositions of iron meteorites. The latest data for iron meteorites provide evidence that accretion and core formation were very short-lived (Kleine et al. 2005a; Markowski et al. 2006; Scherstén et al. 2006). In some cases planetesimal cores formed within 500,000 years of the start of the solar system (Fig. 2) (Markowski et al. 2006). Therefore, they too appear to represent examples of early planetary embryos, as predicted from dynamic theory.

Although there are variations, most giant impact simulations provide evidence that the Moon formed after the Earth had achieved approximately 90% of its current mass. From the W isotopic compositions of lunar samples it has been possible to determine that the Moon must have formed tens of million of years after the start of the solar system (Lee et al. 1997, 2002; Kleine et al. 2005b). All of these approaches yield similar time-scales of between about 30 and 55 Myrs after the start of the solar system providing strong support for the giant impact theory since such a late origin for an object of the size of the Moon is not readily explicable unless it formed from a previously formed planet.

3.4 Core Formation, Accretion and the Early Earth

Mechanisms of core formation were originally based on the concept of metal segregation from a fully formed Earth via inter-granular percolation (Rushmer et al. 2000) and descending diapirs (Stevenson 1990). In a similar vein the models upon which we base our many ideas of partitioning of trace elements in a magma ocean assume a fully formed Earth undergoing metal segregation. Although these models form the backbone of thinking about the physical and chemical processes by which the Earth's core was formed, collisions between differentiated planetesimals and planets would result in core growth by core–core mixing (Yoshino et al. 2003; Halliday 2004).

These effects also will affect Hf/W chronometry. In calculating the time scales for the accretion of the Earth it is assumed that the entire W that is accreted is on average of chondritic composition. This bit is fine because planetary bodies are close to chondritic in Hf/W. However, it is also assumed that this composition mixes and isotopically equilibrates with the W in the silicate Earth. If instead a fraction of the incoming W is in metal from the impactor's core and this mixes with the metal in Earth's core, then the ^{182}Hf–^{182}W "age" of the Earth or its core will appear older than it really is (Halliday 2004).

The Pb isotopic composition of the silicate Earth, as estimated by various authors, plots to the right of the Geochron that defines the age of the solar system (Fig. 3). The standard explanation for this is that the Earth or its core formed late. Both U/Pb and Hf/W are fractionated by core formation because the parent is lithophile, whereas the daughter is siderophile or chalcophile. Therefore, if the Pb isotopic composition of the silicate Earth is modeled in the same manner as the W isotopic composition it should yield a similar result.

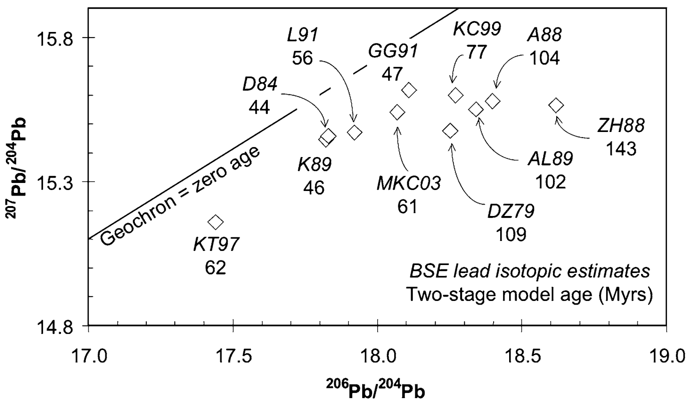

Fig. 3 Estimates of the lead isotopic composition of the bulk silicate Earth (BSE) plotted relative to the Geochron defined as the slope corresponding to the start of the solar system. All estimates plot to the right of this line. If any of these are nearly correct, they provide evidence of protracted accretion or core formation, or both. The times indicated in Myrs are the two-stage model ages of core formation assuming the same values for bulk earth parameters given by Halliday (2004) and Wood and Halliday (2005). Data from Doe and Zartman (1979), Davies (1984), Zartman and Haines (1988), Allègre et al. (1988), Allègre and Lewin (1989), Kwon et al. (1989), Liew et al. (1991), Galer and Goldstein (1991), Kramers and Tolstikhin (1997), Kamber and Collerson (1999), and Murphy et al. (2003). (Full references in Halliday 2004.) These Pb isotope estimates are all significantly longer than the ^{182}Hf–^{182}W estimate of 30 Myrs (Kleine et al. 2002; Yin et al. 2002) which may relate to the differing partitioning of W versus Pb during core segregation of metal versus sulphide (Wood and Halliday 2005)

When these two chronometers are compared a variable but uni-directional offset is found between the timing that is based on W and those based on any of the 11 estimates of the Pb isotopic composition of the silicate Earth (Fig. 3). For example, the two-stage ^{182}Hf–^{182}W model age of the Earth is 30 Myrs whereas the same model applied to $^{235/238}$U–$^{207/206}$Pb yields ages ranging between >40 and >100 Myrs (Fig. 3). It is of course possible that all the Pb isotope estimates are wrong. Given the difficulty with defining a meaningful average for the silicate Earth this is certainly a possibility. However, it is also a finding that is consistent with latest thinking on Earth's oxidation during growth. The transfer of W and Pb to the core may have changed, but not together, during the accretion history of the Earth (Wood and Halliday 2005). Tungsten is moderately siderophile but not chalcophile. The opposite is true for Pb. Sulfides would have formed following the cooling of the Earth after the Moon-forming impact. Removal of lead sulfide to the core may have been responsible for a late-stage increase in U/Pb that defines the Pb isotopic compositions observed. This being the case, the Pb isotopic composition of the bulk silicate Earth provides information on the time scales over which the Earth cooled following the Moon-forming impact. Very roughly speaking the Earth's upper mantle appears to have cooled from temperatures of about 7000 K at the time of the giant impact to about 3,000 K when sulphide would have become stable. The time scales inferred depend on which Pb isotopic estimate is deployed. However, they are all of the order of tens of millions of years after the Moon-forming impact.

3.5 The Age of Heroes

The gravitational energy released assembling Earth is roughly equal to what Earth receives from 200 million years of sunlight. But unlike sunlight, accretional energy arrived in hot lumps. During the hypothetical runaway phase the impacts must have come so frequently that the accretional pulses would have overlapped, with the individual heating events merging into a single geothermal heat flow that for climatological purposes would be like sunlight welling up from below. To this we add radioactive heating. Runaway accretion is fast enough that the short-lived radionuclides ^{26}Al and ^{60}Fe (half lives of 0.7 and 1.5 Myr, respectively) were still abundant. At their initial solar system abundances, radioactive aluminum and iron provide more heating to a Mars-size planet than does accretion. Even if runaway accretion were delayed 2 Myr, radioactive heating would still be comparable to accretional heating for a Moon-size body. Radioactive heating is most potent in small bodies that cannot cool effectively by solid state convection (Woolum and Cassen 1999). If the world is too large, radioactive heating by itself will not melt it (Stevenson 1983).

After a few million years the Sun is faint, short-lived radionuclides are no longer important, and collisions between protoplanets, although bigger than during runaway growth, are well separated in time. This is a different thermal regime. There is no way to spread accretional energy evenly over tens of millions of years. What happens instead is that most of the energy of the giant impacts is quickly radiated to space. After each giant impact the surface gets briefly very hot, but after a million years or so it cools to a point where the energy budget is again dominated by sunlight. If water is abundant, the cooling protoplanet spends some time after each impact perched in a runaway greenhouse state (Abe et al. 2000). For a planet the size of Earth struck by a planet the size of Mars the hot times can last for more than a million years (to be discussed in the following), with the duration depending on the energy of the impact and on the input from the Sun. With the background energy budget set by the (usually) faint Sun, a planet at Earth's distance should have frozen to an ice world if there weren't also an atmospheric greenhouse effect enormously stronger than that enjoyed by Earth today.

Another aspect of the giant impact phase of accretion is that more than half of the collisions are bounces rather than mergers (Agnor and Asphaug 2004; Asphaug et al. 2006). Bounces and mergers both can cause the loss of volatile materials, including geochemical volatiles. Impacts are especially prone to expel exposed surface materials; for example, a differentiated crust of an airless and oceanless planet. Thus there might be an expectation that depletions should depend on geochemical incompatibility or density. Here expectation meets mixed success. There is little evidence that refractory incompatible lithophile elements are depleted in Earth—excess ^{142}Nd might qualify (Boyet and Carlson 2005). But sorting by density between silicates and iron is obvious. In the extreme case one expects a planet like Mercury, where even the silicates have been lost relative to iron (Benz et al. 1988).

The heroic age of accretion ends with the Moon-forming impact. Although it was probably not the last big impact, it was probably the last time that Earth was hit by another planet.

4 Origin of the Atmosphere

Earth's atmosphere is often described as secondary, a choice of words that implies a history. The vanished primary atmosphere is defined as an atmosphere captured from the gases of the solar nebula, presumably by gravity. A primary atmosphere is overwhelmingly hydrogen. Other volatiles are present as hydrides (Urey 1951). Jupiter provides an example. It has been shown that a cool reduced primary atmosphere provides a good substrate for prebiotic chemistry (Miller 1953). Smaller planets like Earth could have captured significant primary atmospheres, depending on how long the nebula lasted (Hayashi et al. 1979; Mizuno et al. 1980; Sekiya et al. 1980a, 1980b, 1981; Sasaki 1990; Ikoma and Genda 2006). A primary atmosphere can be hot enough to melt the surface. Hayashi et al. (1979) showed that the surface temperature of a primary atmosphere of an Earth-mass planet would have been ∼4,000 K, scaling as the two-thirds power of the planet's mass. More recently Ikoma and Genda (2006), using more realistic opacities, revised the theoretical surface temperature of Earth's primary atmosphere downward to ∼3,000 K.

By hypothesis the secondary atmosphere was degassed from the solid Earth after the primary atmosphere was lost. In extreme form, a secondary atmosphere presumes that all Earth's volatiles were accreted in solid bodies akin to meteorites and were later degassed into a primordial vacuum after Earth heated up. In this way the idea that the oceans slowly grew over billions of years first got lodged in textbooks.

Traditional arguments for and against a primary atmosphere are based on the abundances of noble gases. Proponents of the primary atmosphere cite the isotopic composition of the noble gases, the presence of ^{3}He and isotopically solar neon inside the Earth (e.g., Harper and Jakobsen 1996), and the large amount of ^{36}Ar in the atmosphere of Venus (e.g., Genda and Abe 2005). Proponents cite isotopic evidence that massive hydrogen escape took place (Sasaki and Nakazawa 1988; Pepin 1991). If nebular gases circulated through the primary atmosphere, the nebula provided a vast reservoir of volatiles to react with the protoplanets embedded within (Lewis and Prinn 1984). A reduced protoplanet can acquire N, C, and S in refractory minerals (e.g., TiN) and so build up as something akin to the enstatite meteorites. Later, after the nebula is gone, hydrogen escape can oxidize the protoplanet.

Arguments against the retention of a significant primary atmosphere are apparent in the overall elemental pattern of the noble gases in planetary atmospheres, which resembles the

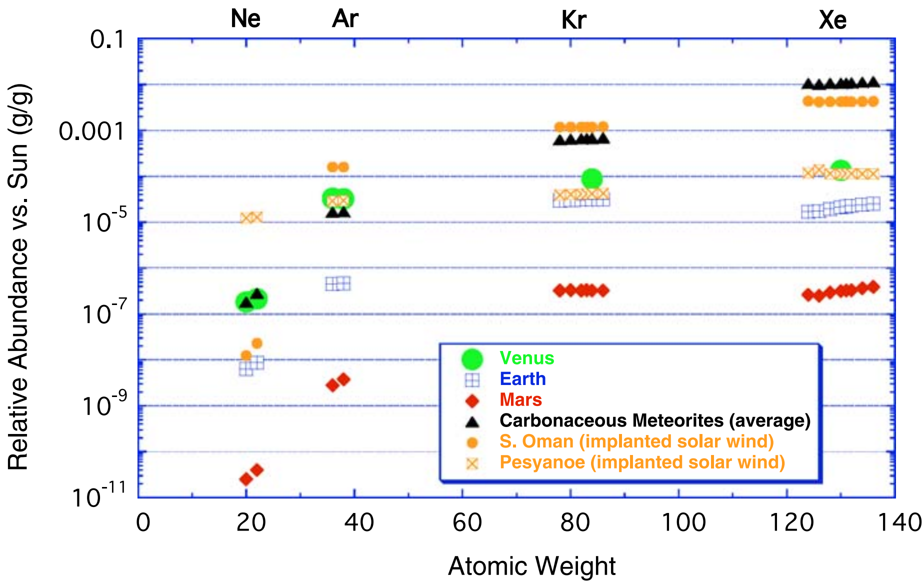

Fig. 4 The abundances of the isotopes of the noble gases (He not shown) relative to their abundances in the Sun. A purely solar abundance pattern would be a horizontal line on this plot. Apart from Xe, the noble gases on Earth and Mars resemble those in carbonaceous meteorites (Pepin 1991), although the planets have less of them. Xenon is discrepant both in quantity and isotopic pattern (which is obviously sloped even on this scale). Venus more closely resembles the implanted solar wind noble gases seen in the meteorites Pesyanoe and South Oman, although the data for Venus are poor (isotope ratios are effectively unconstrained, Kr is very uncertain, and Xe is an upper limit)

elemental pattern seen in meteorites better than it resembles the elemental pattern seen in the Sun, and the extremely low abundance of neon in the atmosphere compared to its abundance in the solar nebula (Fig. 4). First, compare Ne to nonradiogenic Ar. The $^{20}Ne/^{36}Ar$ ratio is >30 in the Sun but is typically ~ 0.3 in planetary atmospheres. Hence, if both Ne and Ar were primary, Ne must have escaped 100 times more efficiently than Ar, and done so from Venus, Earth, Mars, and (apparently) even from the carbonaceous chondritic asteroid parent bodies (Mizuno and Wetherill 1984). Second, compare neon to nitrogen, which is the most volatile element apart from H and the noble gases. The solar N/Ne ratio is unity. In Earth's atmosphere that ratio is 86,000. Either Ne escaped 86,000 times faster than N, or the major source of N was in a condensate of some kind.

The failure of a primary atmosphere to account for neon does not mean that a secondary atmosphere degassed from the mantle into a vacuum. Most volatiles accreted to Earth in solids would have entered the atmosphere directly on impact (Jakosky and Ahrens 1979; Lange and Ahrens 1982; Ahrens et al. 1989). This would generally be the case for asteroids and meteors once collision velocities became high enough, and it would probably be the case for comets at pretty much any collision velocity. Moreover escape to space has been pervasive, and selective enough to affect every isotope differently (next section).

Cold comets provide a variant on the impact-degassed atmosphere. Cold comets are, by construction, low-temperature condensates from the solar nebula. Temperatures are presumed low enough that only H_2, He, and Ne fail to condense in significant quantities. There is evidence that such comets exist now and once existed in large numbers. The most impressive argument is Jupiter's across-the-board volatile enrichment (Owen et al. 1999). Dynamical arguments suggest that such comets are unlikely to have contributed significantly to the C, N, or water inventories of the terrestrial planets, unless they did so in the presence of the solar nebula before Jupiter was fully formed, but they could have supplied the noble gases (Zahnle 1998). Presumably these frosty comets would have degassed their volatiles directly to the atmosphere on impact.

Impact degassing has a velocity threshold that is high enough that it occurs only after planet-sized bodies have formed. Impact degassing is unlikely to have been efficient during the runaway phase of protoplanet growth. On the other hand, the first-generation protoplanets grew so quickly that many of them melted. Thus we might expect general degassing to occur from the first generation of protoplanets simply because they were hot. The net effect is that even the planetary embryos probably had atmospheres and, if far enough from the Sun, hydrospheres. Because these protoplanets were small, once the nebula cleared and they became exposed to the Sun they would have suffered terrible volatile losses to space. It is possible that some of the signatures of atmospheric escape that we perceive in the atmospheres of the planets were established very early in the life of the solar system in the atmospheres of long-vanished little earths.

4.1 Escape and the Noble Gases

The active young Sun was a powerful source of ultraviolet radiation (Fig. 1). Far UV wavelengths between 100 and 200 nm are absorbed by water and CO_2 and cause these molecules to break up into atoms or into simpler, more transparent molecules such as H_2 and CO. The survivors are in general poor infrared coolants. The more energetic Extreme UV ($\lambda < 100$ nm) is strongly absorbed by everything. Absorption takes place at very high altitudes where, if the FUV and EUV fluxes are big, only poor infrared coolants remain. Some of these matters are discussed in the chapter by Kulikov et al. (2007, this issue). Without effective coolants the EUV makes the thin gas very hot, and if hydrogen is relatively abundant the gas can satisfy conservation of energy by driving a wind of hydrogen into space. This is called hydrodynamic hydrogen escape and it appears to have been an important process in sculpting the atmospheres of the terrestrial planets (Sekiya et al. 1980ba, 1981; Watson et al. 1981).

Evidence that Earth experienced vigorous hydrodynamic hydrogen escape is preserved in the mass fractionated isotopes of neon and xenon. Mantle neon is isotopically lighter than atmospheric neon; this can be readily explained by escape (Ozima and Podosek 2002). Xenon is more interesting because it is the heaviest gas found in the atmosphere. Yet atmospheric xenon is strongly mass fractionated compared to any of its plausible solar system sources (Fig. 4). In principle vigorous hydrodynamic hydrogen escape can produce the observed isotopic fractionation (Sekiya et al. 1980b; Zahnle and Kasting 1986; Hunten et al. 1987; Sasaki and Nakazawa 1988; Pepin 1991). The required hydrogen flux is high but within the range permitted by EUV emission from the active young Sun. However, the model predicts that gases lighter than Xe (i.e., all of them) should also escape. But krypton is not mass fractionated, and it is relatively more abundant than xenon. How might xenon escape leaving krypton behind? Sasaki and Nakazawa (1988) and Pepin (1991) suggested that fractionated xenon is a remnant of the lost primary atmosphere. Argon and krypton are later replenished by degassing from the planet's interior (i.e., they are secondary), but xenon in the Earth is presumed to enter the core or into high-pressure silicates. Another possibility is that xenon escaped as an ion. Xenon is the only noble gas more easily ionized than hydrogen. In a hydrogen wind Xe would be ionized but Kr would not. If hydrogen ions escaped, as would be possible along open magnetic field lines, strong Coulomb interactions would drag any other ions along. In this way Xe can be the only noble gas to escape.

Radiogenic xenon supplies two additional arguments for large-scale escape. Some 7% of atmospheric ^{129}Xe is from the decay of radioactive ^{129}I (half-life 15.7 Myr). The atmospheric inventory of radiogenic ^{129}Xe is about 0.8% of what it should be given the primordial abundance of ^{129}I in meteorites. This means that, over the course of accretion, Earth and the protoplanets, planetesimals, km-size bodies, loose boulders, grains and dust motes that built it lost 99.2% of their ^{129}Xe (Porcelli and Pepin 2000).

Another radiogenic xenon is the product of spontaneous fission of the very nearly extinct ^{244}Pu (half-life 81 Myr). Plutonium was never abundant but its abundance in primary solar system materials is known. Fission yields a spectrum of neutron-rich daughter nuclei. Five xenon isotopes—129, 131, 132, 134, 136—can be produced this way. It is difficult to separate ^{244}Pu fission products in air from nonradiogenic xenon in air, or from confusion with the similar products from spontaneous fission of ^{238}U, but fissogenic Xe is seen unambiguously in mantle samples. The interesting point is that most of the fission xenon is missing from the atmosphere (Ozima and Podosek 2002, pp. 235–241). For the atmosphere we have two model-dependent estimates that a disinterested student can regard as upper limits. Expressed in terms of ^{136}Xe (the most fissogenic xenon isotope), Pepin (1991) concluded that 4.6% of the ^{136}Xe in air is fissogenic, while Igarashi (1995) found that 2.8% is fissogenic. Both models have questionable features. Pepin (1991) made use of a hypothetical primordial xenon ("U–Xe") that is distinctly depleted in fissogenic isotopes when compared to solar wind samples, while Igarashi (1995) treated the composition of fissogenic isotopes as unconstrained by the known fission yields from ^{244}Pu or ^{238}U. This problem is currently unresolved. But even Pepin's fission xenon is only 30% of what we would expect of a thoroughly degassed mantle with chondritic Pu. It is possible that Xe was still being lost (either to space, the core, or the deep mantle) more than 200 million years after the meteorites were made.

4.2 Water

The most probable original source of Earth's water was ice, either condensed locally in the planetesimals from which the bulk of Earth was made (Abe et al. 2000), or in more distant planetesimals scattered from what is now the asteroid belt (Morbidelli et al. 2000; Raymond et al. 2004), or in comets. This is not to say that this water was in the form of ice when it reached the Earth. Rather, much of the water was in the form of hydrous silicate minerals. Chemical reactions between silicates and meltwater inside the planetesimals were the source of the hydrated silicate minerals that are abundant in many meteorites (Bunch and Chang 1980). Other possible sources of water involve oxidation of organic molecules or of primary H_2 (Abe et al. 2000). If the water came in planetesimals, either of local origin or from the asteroid belt, the water came with the building blocks of the Earth, and therefore likely predated the Moon-forming impact. Dynamical simulations (Levison and Duncan 1997; Levison et al. 2001) show that after Jupiter formed the chance that an object from the outer solar system hits Earth is $\sim 3 \times 10^{-7}$. This means that an outer solar system source of water either predated the formation of Jupiter (and therefore predated the Moon-forming impact), or that by happenstance Earth was struck by a Pluto-sized body. If there were once 10^4 Plutos (the summed masses of Uranus and Neptune), the chance that a Pluto hit Earth after Jupiter formed is only $\sim$0.3%. The odds favor water's co-accretion.

5 After the Moon-Forming Impact

The Moon-forming impact is presently thought to have occurred at around 30–50 Ma (Fig. 2). By coincidence the Sun reached the main sequence ∼50 Ma (Fig. 1). This is a good place to take up Earths' story.

Most of the mantle was melted by the Moon-forming impact, and ∼20% was vaporized (Stevenson 1987; Canup 2004). Strong heating occurred extensively: throughout the hemisphere that was hit, everywhere in the upper mantle where impact ejecta fell back into it, and in the deep mantle because of the energy released by merging the two planets' cores. If appreciable solid mantle survived the impact it probably sank into contact with the hot core and was melted. Canup's (2004) simulations show large parts of the mantle heated by less than 1,000 K, large parts of the mantle heated by more than 4,000 K, and substantial mantle heated to all temperatures in between. She also found that the surface is hottest (∼8,000 K), with the silicates captured from Theia being especially hot. Even higher temperatures are found at the top of the core, mostly in materials that came from Theia's core. That Theian materials would be especially hot on Earth is unsurprising given their high pre-impact kinetic energies (as measured against the center of mass frame).

The Moon-forming impact may or may not have expelled a significant fraction of Earth's pre-existing volatiles, and the Earth may or may not have had abundant volatiles to lose. It is generally agreed that the volatiles on the side of Earth that got hit were lost, but it is an open question how volatiles on the other side could be lost. Theory suggests that the answer depends on whether there had been a deep liquid water ocean on the surface. It is possible that a thin atmosphere over a thick water ocean could be expelled. Otherwise the atmosphere is retained (Genda and Abe 2003, 2005). One notes that water is retained in either event. The view taken here is that the proto-Earth did have water oceans (cf. Abe et al. 2000) and that the atmosphere was incompletely expelled.

Canup's numerical simulations give no indication that significant escape from Earth occurs in the Moon-forming impact. At 8,000 K there would be some thermal escape, but radiative cooling is extremely competitive: it takes less than a day to cool 100 bars of silicate vapor at 8,000 K. On such prompt time scales escape is possible only if the gas carries within it all the energy it needs to escape. At 8,000 K this implies that a quantitatively escaping gas would have to have had a mean molecular weight of less than 3, which is plausible for a hydrogen atmosphere but unachievable otherwise. Thus a giant impact provides thermal energy sufficient to dissipate a primary atmosphere but not enough to dissipate a secondary atmosphere. Such events are too abrupt to produce isotopic fractionation. Presumably Earth's primary atmosphere was removed by an earlier giant impact long before the Moon was made.

5.1 A Fog of Rock Vapor

Once the atmosphere settled down it was mostly rock vapor topped by silicate clouds at ∼2,500 K. For a thousand years the silicate clouds defined the visible face of the planet. The Earth might have looked something like a small star or a fiery Jupiter wrapped in incandescent clouds. Silicates condensed and rained out at a rate of about a meter a day. Mixed into the atmosphere, at first as relatively minor constituents but becoming increasingly prominent as the silicates dropped out, were any volatiles initially in the mantle plus the air that survived the impact. Because convective cooling requires that every parcel be brought to the cloudtops to cool, it seems likely that the mantle would have degassed. This phase is labeled "rock vapor" in Fig. 5.

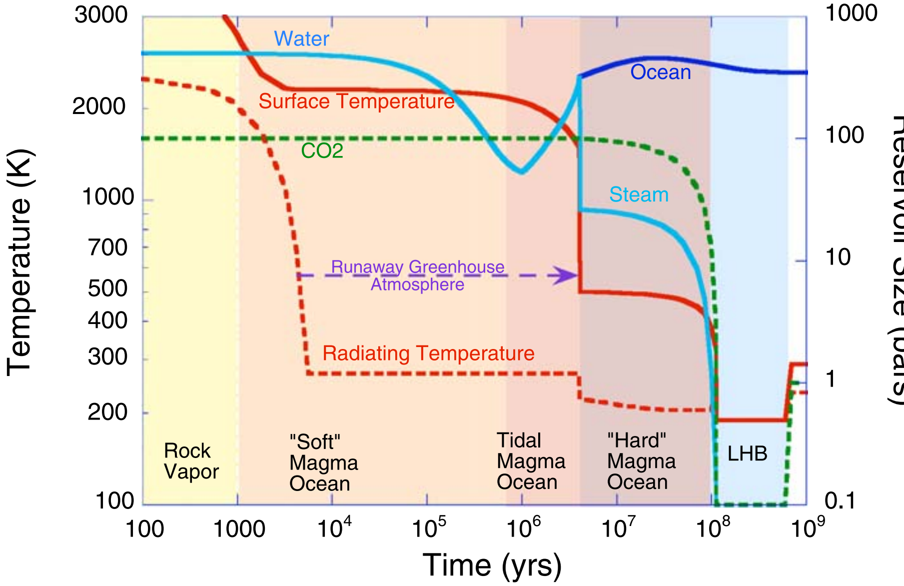

Fig. 5 A cartoon history of temperature, water, and CO_2 during the Hadean. The Hadean begins with the Moon-forming impact. For 1,000 years Earth is enveloped in rock vapor. CO_2 and other gases are presumed to degas from the convecting silicate gas, while water mostly partitions into the interior. A substantial greenhouse effect and tidal heating maintain the magma ocean for some 2 million years. Most of Earth's water and the rest of the CO_2 degassed as the mantle solidified. After the mantle solidified the steam atmosphere condensed to form a warm (∼500 K) water ocean under ∼100 bars of CO_2. This warm, wet early Earth would have lasted while Earth's CO_2 stayed in the atmosphere. In this illustration CO_2 is assumed to subduct into the mantle on either a 10 Myr (*solid curves*) or a 100 Myr (*dotted curves*) time scale. The asymptotic CO_2 partial pressure is assumed to be controlled at low levels by chemical weathering of oceanic crust and abundant ultramafic impact ejecta. Prior to the origin of life, in the absence of an abundant potent greenhouse gas, the surface should have been ice covered and very cold, although occasional impacts brought brief thaws. Finally, after the late bombardment, the CO_2 is allowed to return to ∼1 bar levels in order that the surface be clement; this too is arbitrary

After the silicates condensed what remained was a hot atmosphere over a deep magma ocean. The composition of the atmosphere in detail depends on the oxygen fugacity of the silicates, the temperature, the solubilities, and the chemical inventories of the different volatile elements (Holland 1984; Abe et al. 2000). Popular buffers are QFM (quartz-fayalite-magnetite) and IW (iron-wustite). The IW buffer is about 100 times more reducing at 1,500–2,000 K (Lodders and Fegley 1998). Elementary calculations (see Holland 1984) indicate that, for an oxygen fugacity bounded by these buffers, the CO_2/CO ratio is between 0.5 and 5 at 1,500 K and between 0.2 and 2 at 2,000 K. Similarly, the H_2O/H_2 ratio would be between 30 and 300 at 1,500 K and between 1 and 10 at 2,000 K. On the other hand, Sasaki (1990) and Abe et al. (2000) both suggested that the ratio of H_2O to H_2 was between 0.1 and 0.3 for IW at 1,500 K, which leaves a hundred-fold disagreement that is hard to understand.

Water is relatively soluble in silicate melt (Holland 1984, pp. 81–82; Matsui and Abe 1986. Holland referred to Rubey 1951; evidently this is not a new idea). As the magma freezes the water is expelled (Zahnle et al. 1988). In preparing Fig. 5 we used a solubility of $x_s = 6 \times 10^{-4}\sqrt{pH_2O}$ (bars) (Zahnle et al. 1988). The square root dependence indicates that H_2O dissolves in silicate as OH^-. For Fig. 5 we partition the water between the mantle and the atmosphere according to the volume of the magma and the fraction of the surface that is liquid.

Other gases are not very soluble in the magma ocean. Holland estimates that somewhat less than half of the CO_2 would go into a wholly molten mantle, and he suggests that other gases, such as H_2, CO, N_2, and the noble gases probably behave similarly. It is possible that this was when the solar component of Earth's noble gases entered the mantle.

To first approximation the major atmospheric constituents over a 2,000 K magma ocean would have been CO, CO_2, H_2O, and H_2, in that order. But as the mantle cooled most of the H_2O degassed and the bigger molecules became relatively more stable, so that at 1,500 K the composition would have become H_2O, CO_2, CO, and H_2 in that order. For simplicity in preparing Fig. 5 we have ignored H_2 and CO.

A silicate vapor atmosphere is hot enough that hydrogen readily escapes to space, although escape is selective. The maximum rate that hydrogen can diffuse through a background atmosphere takes the form of a flux, usually called the diffusion-limited flux, that sets the limit to selective escape (Hunten and Donahue 1976; Zahnle and Kasting 1986). Among other things, the diffusion-limited flux sets an upper limit on how quickly hydrogen can be separated from oxygen. For example, for Earth or Venus, it takes at least 20 million years to separate the hydrogen from the oxygen in an ocean of water. Over 1,000 years this is obviously a negligible amount of oxidation. Over 2 million years Earth might lose as much as 10% of its hydrogen. For our purposes this is probably negligible; in any event we still have enough. But one hesitates to say the same for Venus, which because of proximity to the Sun spends more time in the runaway greenhouse state. The lead author (for one) suspects that hydrogen escape may have doomed Venus very early. For hydrogen escape to play a significant part in oxidizing the Earth it needs to have taken place over many tens or hundreds of millions of years while Earth was more-or-less normal.

The post-silicate atmosphere may also have contained moderately volatile elements such as cadmium. The most abundant of these are S, Na, Zn, Cl, and K. These may not fully condense until after the magma ocean freezes. We might therefore expect the first crust to be enriched in these elements. Mass balance would imply an early chalcophilic crust a few km thick. Presumably the hot new ocean would interact with the crust preferentially. A salty sea seems slated from the start.

5.2 Steam Atmospheres and Magma Oceans

While the magma ocean was everywhere hotter than the liquidus convective cooling was extremely fast (Abe 1993; Solomatov 2000). A crude estimate of the thermal energy available to the magma ocean is to assume that the whole mantle was on average 800 K hotter than the liquidus (roughly the difference between the condensation temperature at the cloudtops and the melting temperature), so that it contained $\sim 4 \times 10^{30}$ J of readily accessible heat. To this can be added another $\sim 2 \times 10^{30}$ J of excess heat in the core. Together these correspond to $\sim$20% of the impact energy, which may be a little high.

Tidal dissipation complicates the budget by providing an energy source that is of the same order of magnitude as the thermal energy. If the Moon formed just beyond the Roche limit (Kokubo et al. 2000), it would have formed at $\sim$3 Earth radii and Earth's day would have been $\sim$5 hours long. The energy dissipated inside the Earth while raising the Moon's orbit provides another 3×10^{30} J. We will return to tidal heating in Sect. 5.2.1.

The rate that Earth cooled after the silicate clouds condensed is determined by thermal blanketing by the atmosphere and by the surface temperature of the magma ocean. Figure 6, adapted from Abe et al. (2000), illustrates the effect. If the surface is cool enough and the

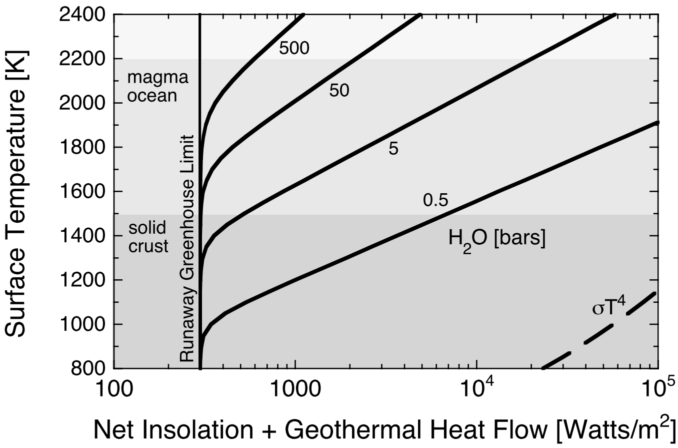

Fig. 6 Radiative cooling rates from a steam atmosphere over a magma ocean. The radiated heat is equal to the sum of absorbed sunlight (net insolation) and geothermal heat flow. The plot shows the surface temperature as a function of radiated heat for different amounts of atmospheric H_2O (adapted from Abe et al. 2000). The radiated heat is the sum of absorbed sunlight (net insolation) and geothermal heat flow. The different *curves* are labeled by the amount of H_2O in the atmosphere (in bars). The runaway greenhouse threshold is indicated. This is the maximum rate that a steam atmosphere can radiate if condensed water is present. If at least 30 bars of water are present (a tenth of an ocean), the runaway greenhouse threshold applies even over a magma ocean. Note that the radiative cooling rate is always much smaller than the σT^4 of a planet without an atmosphere

atmosphere thick enough, the thermal blanketing can be extremely effective. But as the temperature increases the atmosphere becomes more transparent to thermal radiation from the surface, and it becomes harder for water to condense. This was shown by Kasting (1988) and by Abe and Matsui (1988) and exploited in some 1980s models of terrestrial planet accretion (Abe and Matsui 1988; Zahnle et al. 1988). If water does condense, then the familiar runaway greenhouse limit applies and the rate of radiative cooling is very slow. A dry atmosphere is not subject to the runaway greenhouse limit because it has already run away.

The atmosphere stays in a runaway greenhouse state while the magma ocean is fluid and the geothermal heat flow is high enough. Given at least 20 bars of water, the surface can be held at the melting point of rock by a stabilizing negative feedback between water vapor's control over the surface temperature and water's solubility in the liquid magma (Abe and Matsui 1988; Zahnle et al. 1988). To illustrate the feedback, add water to the atmosphere. This raises the surface temperature. The fraction of the surface covered with liquid magma increases. Hence more water dissolves in the magma, and the extra water is removed from the atmosphere.

Once water condensed the atmosphere entered the runaway greenhouse state[3], in which thermal radiation is emitted to space at a fixed rate of $\sim$310 W/m^2 (Fig. 6) set by the physical and optical properties of water (Kasting 1988; Abe 1988). For 500 bars of water (which, including the mantle, approximates Earth's total inventory today), water begins to condense

[3]The usual runaway greenhouse refers to the response of a wet planet to too much sunlight, in which case the oceans evaporate into steam. It can be told as a cautionary tale: "Don't go too close to the Sun, or you'll end up like Venus." In detail the runaway greenhouse is best understood in terms of the thermal radiation a planet emits to space. The "runaway greenhouse limit" refers to the particular rate of thermal emission where the phase change between oceans and steam takes place.

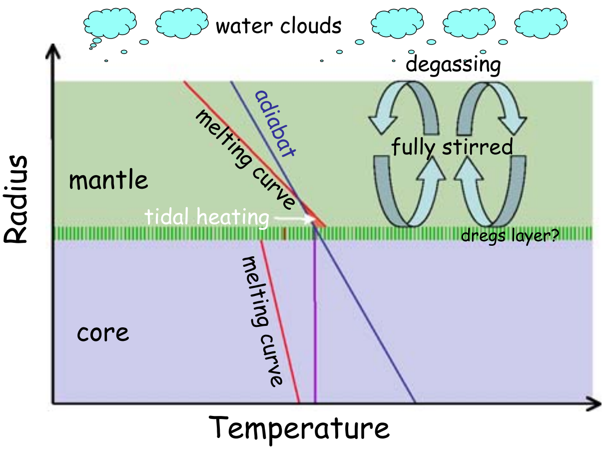

Fig. 7 A cartoon illustrating conditions inside the Earth ca. 1 million years after the Moon-forming impact. Schematic adiabats and melting curves are indicated. Tidal heating is concentrated at the base of the mantle. The mostly liquid mantle is probably fully stirred and equilibrated with the atmosphere. Temperature in the mantle follows the adiabat. At this early time the core is liquid but probably not convective. It is more likely that is heated from above by conduction. Therefore there is no reason to expect a substantial magnetic field. Slag layers may form at the top and bottom of the mantle

when the surface temperature drops below 1,800 K (Fig. 6). Absorbed sunlight provides 120–170 W/m^2, depending on the albedo. The difference, 140–190 W/m^2, is made up by the geothermal heat flow associated with secular cooling[4]. If water is not the most abundant gas, the runaway greenhouse threshold can rise to ∼400 W/m^2 (Nakajima et al. 1992), for which the geothermal heat flow would be 230–280 W/m^2. If there is less than 20 bars of water, water does not condense until after the magma ocean has frozen, but this is not a plausible state for Earth. For specificity we will use 140 W/m^2 (equivalent to a 30% albedo) as the amount of geothermal heat flow required to maintain the runaway state.

5.2.1 Tidal Heating

The mantle freezes from the bottom up because the melting curve is steeper than the adiabat. This is illustrated by Fig. 7. Consequently tidal heating is concentrated at the bottom of the mantle. Fast-growth of Rayleigh–Taylor instabilities guarantees that the mantle's temperature profile obeys the adiabat (Solomatov 2000).

Viscous damping of tidal motions generates heat. Therefore tidal heating occurs most strongly in materials that are solid but close to melting. This introduces the possibility of a governing feedback that works through the dependence of viscosity on temperature. If tidal dissipation exceeds what the atmosphere can radiate, the excess heat raises the temperature, which lowers the viscosity, which in turn lowers the rate of tidal dissipation. This looks like a stable feedback.

It follows that, while tidal dissipation was important, the base of the mantle was solid but the rest of it was fluid, and tidal heating generated almost all of the thermal energy radiated to space. In the limit of an asymptotically thick steam atmosphere, tidal dissipation would have been regulated to generating heat at the runaway greenhouse limit of ∼140 W/m^2.

The runaway greenhouse limit is a good approximation as the magma ocean cooled, but it is not as good an approximation when the magma ocean was much hotter than the liquidus and most of the water was dissolved in the melt. In preparing the mantle cooling history

[4]If the geothermal heat flow is too low to support the runaway greenhouse, rain falls, oceans accumulate, and the surface of the mantle would be cold. A cold surface contradicts the assumption of a liquid magma ocean.

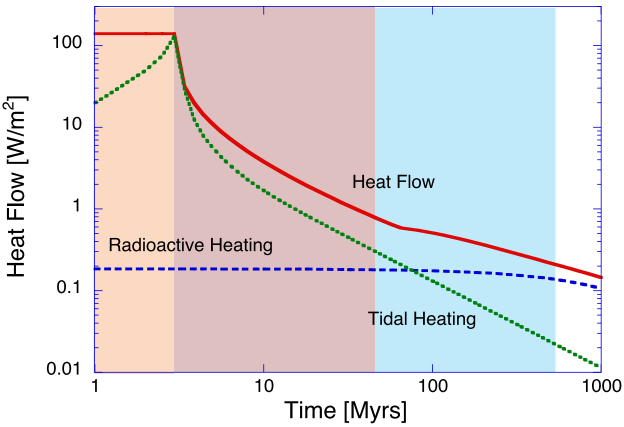

Fig. 8 A cartoon history of mean heat flow during the first billion years after the Moon-forming impact. Epochs correspond to those in Fig. 5. Tidal heating plays an important role in prolonging the magma ocean. Tidal forcing wanes as the Moon evolves away from the Earth. Thereafter heat flow is controlled by convection of the solid mantle. By 4.4 Ga the global average heat flow would have been ~0.5 W/m^2. Later in the Hadean typical heat flows would have been 0.2–0.3 W/m^2, not enormously larger than what they are now. For comparison heat flow today is 0.065 W/m^2 through the continents and 0.1 W/m^2 through the ocean crust. Computational assumptions are given in the text

shown in Fig. 5 we have self-consistently used (1) the cooling rates from Fig. 6; (2) water's solubility in liquid basalt; (3) assumed that water is confined to the molten fraction of the mantle; (4) assumed a total Earth inventory of 500 bars of water; and (5) assumed a heat capacity of 1.2×10^7 ergs/g/K and a heat of fusion of 4×10^9 ergs/g for the melt. Tidal heating was arbitrarily concentrated toward the beginning of the magma ocean.

In this model, after ~1.4 million years the Moon will have evolved far enough away from the Earth that tidal dissipation[5] drops below the ~140 W/m^2 threshold. Thereafter secular cooling takes over, and a freezing front rises through the mantle until it reaches the surface. This transition marks the end of the liquid magma ocean (Fig. 5). As the mantle freezes the solubility feedback tries to keep the surface molten by degassing water. In some models most of Earth's water is degassed in a terminal event like this (Zahnle et al. 1988). But once the mantle solidified heat flow fell under rheological control (Solomatov 2000), dropping to (unknown) levels well below those required to sustain a runaway greenhouse atmosphere (Fig. 8). Thereafter water condensed and rained out at ~1 meter per year until the oceans returned[6].

In preparing Fig. 5 we assume that heat flow decays inversely as the one-third power of viscosity after the collapse of the runaway greenhouse. This is like conventional parameterized convection in the limit that the only temperature dependence to matter is viscosity's. Viscosity varies by at least 15 orders of magnitude over a small temperature range when near the solidus (Liebske et al. 2005). We arbitrarily assume that viscosity is an exponential function of temperature, with e-folding scales of 43 K below the solidus and 3.3 K above the

[5]For conservative values of the quality factor Q. Q is the ratio of power in the tides to dissipation. Low Q implies lossy tides.

[6]The net rainfall rate of ~1 m/yr refers to the global mean difference between rainfall and evaporation. It is not obvious what a rain gauge would report. Ishiwatari et al. (2002) computed average rainfall rates exceeding 10 m/yr in a GCM study of a runaway greenhouse atmosphere, but their simulated climates are far out of balance, and feature cold poles and a lot of hot, dry air. A passively cooling steam atmosphere may be too bland to demand heavy rain.

solidus. The heat capacity of the mantle is taken as 6×10^{27} J/K and 1.4×10^{28} J/K below and above the solidus, respectively. The latter takes into account latent heat of fusion. The core is ignored, although it was probably a significant heat source to the mantle on these time scales. Radioactive heating is 0.2 W/m^2 using conventional K, Th, and U abundances. Tidal heating is estimated using a "Q" value that is at first 10-fold more dissipative than Io's (where $Q = 36$, Schubert et al. 2001), and which linearly increases to Io's value as the Moon's orbit expands to half its current distance. These assumptions take their cue from our sense that tidal dissipation ought to have been most efficient before the mantle hardened. An illustrative thermal history is presented in Fig. 8. The mantle reaches the solidus at 20 Myr. Global heat flow is 0.5 W/m^2 after 100 Myr and drops to 0.2 W/m^2 by the end of the Hadean. For comparison, heat flow on Io is 2.0 W/m^2 (Spencer et al. 2000).

The mantle volatile content is set by the solubility (in the melt) or the stability (of minerals in a solid) at the surface, at least while the mantle is strongly convective. The surface acts like a cold trap, and while the mantle remains strongly convective, every parcel visits the surface. What this means for water is that, if hydrous minerals are unstable at the surface, even the deep mantle dries out, irrespective of the stability of water-bearing minerals at high pressure. What this means for gases that are sparingly soluble in the melt is that they degas as the mantle freezes. Hence the gases that were left behind in the mantle represent a small sample of the atmosphere at the time of the last major magma ocean.

The argument that the mantle should rid itself of water and other volatiles as it froze implicitly assumes whole mantle convection. If instead the young mantle convected in separate layers such that the deep mantle was isolated, the greater stability of hydrous phases at high pressure may be relevant. This opens the possibility that substantial amounts of water, initially incorporated as solute, could be stored indefinitely in the lower mantle. Later, when layered convection broke down, the stored water would emerge and be degassed. In this way it is possible for the oceanic volume to grow over time. Such a model must make a host of other predictions. Conventional layered convection, in which the lower mantle remains convectively isolated over the whole history of the planet, renders the composition of the lower mantle irrelevant to the history of volatiles at the surface.

5.2.2 History of the Lunar Orbit

The history of the lunar orbit has been lucidly discussed many times (Goldreich 1966; Touma and Wisdom 1994, 1998). Figure 9 is not a substitute for these studies. Rather it merely shows the distance to the Moon and the length of the day during the Hadean for the tidal heating history shown in Fig. 8. Figure 9 assumes a circular orbit and conservation of angular momentum of the Earth–Moon system.

The lunar orbit is inclined by $\sim 5°$ to the ecliptic. Integrations of the lunar orbit backward in time indicate that the 5° inclination to the ecliptic today maps directly into a $\sim 10°$ inclination to Earth's equator when the Moon was near Earth (Goldreich 1966; Touma and Wisdom 1994). An inclined birth-orbit is deeply puzzling, because the giant impact origin of the Moon generates the Moon from a debris disk that revolves in the Earth's equator, and the disorderly precession of inclined orbits causes collisions that ultimately drive all the debris into orderly equatorial orbits.

Touma and Wisdom (1998) suggested that the Moon acquired its inclination via two resonances that occur early in the evolution of the lunar orbit. The first of these occurs when lunar perigee precesses with a period of one year (the resonance is between perigee and perihelion). This resonance pumps up eccentricity. The second resonance is between the year and the combined precessions of perigee and the Moon's inclination with respect to Earth's equator. This resonance converts eccentricity into inclination.

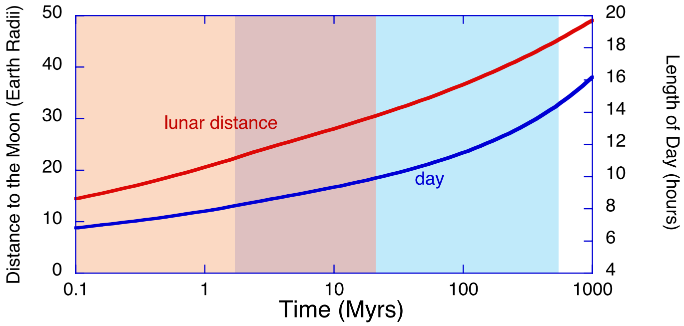

Fig. 9 The distance to the Moon and the length of Earth's day in the Hadean after the Moon-forming impact. Here the rate of evolution is at first controlled by the runaway greenhouse effect. This is 100–1,000 times slower than tidal evolution would be in the absence of an atmosphere (cf. Touma and Wisdom 1998)

To capture the lunar orbit in these resonances requires that the lunar orbit evolve at least 2 orders of magnitude slower than conventional models predict. Thermal blanketing by a steam atmosphere can do this. At the runaway greenhouse limit, tidal evolution is slowed by 3 orders of magnitude compared to conventional models. Thermal blanketing also unbalances the rates of tidal dissipation in the Earth and Moon, which meets another of Touma and Wisdom's (1994) requirements. Thus the history of the lunar orbit both sets a lower limit on the duration of Earth's magma ocean and suggests the presence of a significant amount of water on Earth at the time of the Moon-forming impact.

5.3 Hot Water

The state of the atmosphere after the deluge depends on how much CO_2 was available. If most of Earth's modern CO_2 inventory were in the atmosphere as CO_2, the surface temperature would have been ~500 K (Fig. 10). Presumably carbonate rock formed quickly, but the capacity of the oceans and ocean crust to store carbonate is limited, and the bulk of the CO_2 remained in the atmosphere until the carbonates were subducted into the mantle or unless or until there were stable continental platforms on which to put it (Sleep et al. 2001).

Today most subducted carbonate enters the mantle rather than erupting through arc volcanoes. Was subduction more efficient in a hot mantle? Higher temperatures made carbonates less stable, but the lower viscosity let foundering crustal blocks sink more quickly. If they sank quickly enough they would have taken their carbonates to the bottom of the mantle, thereby scavenging the atmosphere of its CO_2.

We follow the discussion of Sleep et al. (2001). It is unlikely that the seafloor itself at any one time could have held more than ~10 bars of CO_2 as carbonates. This estimate comes from assuming that the seafloor is ultramafic and hydrothermally altered to a depth of 500 m, and that most of the available cations were used to make carbonates. This is a small fraction of the >100 bar planetary inventory. At some stage—after 20 million years in the cartoon—global heat flow waned to 1 W/m^2. This crust would have resembled 1 Ma ocean crust on Earth today. It was a significant CO_2 sink. Carbonate now forms within the uppermost hundreds of meters of young oceanic crust. If there was no CO_2 degassing from foundered crust, the global resurfacing time of 1 Ma implies that it could have taken as little as 10 Ma to remove 100 bars of CO_2 from the atmosphere and inject it into the mantle. How long it actually took to remove the CO_2 depended on how efficiently carbonate was subducted. For specificity in preparing Fig. 5 we assume this takes either 10 Myr or 100 Myr, but we cannot

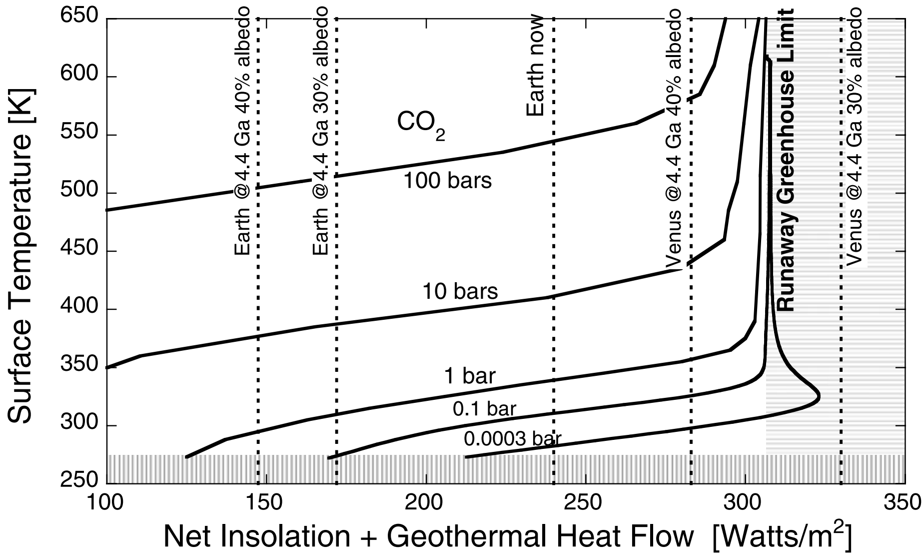

Fig. 10 The H_2O–CO_2 greenhouse. The plot shows the surface temperature as a function of radiated heat for different amounts of atmospheric CO_2 (after Abe 1993). The albedo is the fraction of sunlight that is not absorbed (the appropriate albedo to use is the Bond albedo, which refers to all sunlight visible and invisible). Modern Earth has an albedo of 30%. Net insolations for Earth and Venus ca. 4.5 Ga (after the Sun reached the main sequence) are shown at 30% and 40% albedo. Earth entered the runaway greenhouse state only ephemerally after big impacts that generated big pulses of geothermal heat. For example, after the Moon-forming impact the atmosphere would have been in a runaway greenhouse state for ∼2 million years, during which the heat flow would have made up the difference between net insolation and the runaway greenhouse limit. A plausible trajectory takes Earth from ∼100 bars of CO_2 and 40% albedo down to 0.1–1 bar and 30% albedo, at which point the oceans ice over and albedo jumps. Note that CO_2 does not by itself cause a runaway. Also note that Venus would enter the runaway state when its albedo dropped below 35%

guarantee that it even happens at all. However, we note that there is no obvious buffer on CO_2 levels other than those producing hot (∼500 K) and cool or cold (∼270 K) climates (Sleep et al. 2001).

By contrast hydrated minerals are not very stable at high temperatures and low pressures. If they survive a fast passage to the mantle they may not have stayed there. They ought to have formed water-rich melts at the base of the magma ocean that ascended as proto-granitic plumes. We therefore expect that water was mostly partitioned into surface reservoirs during the magma ocean, and that the early oceans were if anything deeper than the oceans later became.

6 Hadean Geography and Geodynamics

Earth today has a global mean heat flow of 0.086 W/m^2, which much exceeds heating by radioactive decay (0.040 W/m^2). The mismatch is even bigger if the continents aren't included in the accounting. The mismatch shows us that mantle convection is not well described by textbook boundary layer theory, which predicts that heating and cooling are nearly equal. To fix this with plate tectonics requires taking the strength of the plates into account (Sleep 2007). When this is done, the model of plate tectonics that gives the observed behavior predicts that heat flow is nearly independent of the mantle's temperature. This has several interesting consequences, including possible non-monotonic thermal histories[7]. Plate tectonics of this kind cannot handle a heat flow much greater than 0.1–0.2 W/m^2 (Sleep 2007). Something else is needed between the end of the magma ocean and the advent of plate tectonics.

Jupiter's volcanically active moon Io provides an interesting albeit imperfect analogy. Io is dry, its surface gravity is only 1.8 m/s^2, and its heat is generated by tides. But the heat flow is big. Io's global mean heat flow is observed to be 2.0 W/m^2 (Spencer et al. 2000). This is higher than what we expect for the Hadean Earth after the first 10 Ma. Io cools itself by lava flows, layer upon layer, each thin and each well cooled. Cooling by flood volcanism is very efficient (Sleep and Langan 1981). The old cold flows sink slowly back into the crust. This leaves a thick cold crust atop a hot mushy ocean (Keszthelyi et al. 1999). Thermal emission indicates that Io's lava flows are very hot when erupted, $>$1,600 K. The high temperature suggests an ultramafic composition (McEwen et al. 1998), which implies that Io's mantle is not highly differentiated (Keszthelyi et al. 1999). In particular Io does not seem to have generated a compositionally distinctive crust of low-melting-point magmas. Cooling by lava flows explains this as well, because differentiation occurs only on the scale of the individual lava flows, which are thin (Sleep and Langan 1981).

We might expect similar behavior on Earth for a few tens of millions of years after the Moon-forming impact when heat flows were still high and tidal heating was still important. A heat flow of 1 W/m^2 equates to a resurfacing rate of $\sim$1 cm/yr (i.e., 100 km in 10 Myr). On Earth the ultramafic lavas would react with abundant water and abundant CO_2 to make hydrous minerals and quite a lot of H_2, and possibly CH_4. When recycled the hydrous ultramafics would make bonanites, and these upon dehydration become dense enough to sink into the mantle, thereby erasing much of the evidence. In any event we do not expect that Earth spent a long time in such a state, assuming that it did enter such a state, because heat flows $>$1 W/m^2 cannot be long sustained given that radioactive heating was only $\sim$0.2 W/m^2 and the Moon was receding.

We speculate that the missing link between Io-like hyperactive volcanism and modern plate tectonics was a basaltic mush ocean about 100 km thick (Fig. 11). Modern fast ridge axes provide an analogy. Magma entering the axis freezes quickly (Sinton and Detrick 1992). The bulk of the "magma" chamber is mostly crystalline mush at the basalt solidus; it is almost melt-free and when fresh flows like a glacier. Only a thin (tens of meters) lens of fully molten rock exists at the axis. The heat flow at the ridge axis can be estimated from the dimensions of the magma chamber, the latent heat of fusion, and the spreading rate (Sleep et al. 2001). The fastest spreading ridge on Earth today corresponds to a heat flow of 40 W/m^2. Such rapid cooling was unsustainable globally for more than a few million years. When the magma ocean froze to mush, it was only a few 100 K hotter than the modern mantle.

The 100 km thickness of the basalt layer is self-regulated by the stability field of garnet, resulting in a phase change that makes pressurized basalt more dense than mantle. The bottom of a thicker pile would spontaneously sink into the mantle. The hot basaltic mush is topped by a colder frozen basaltic crust. In a thick mush ocean the material is solid by the time it sinks to the base of the ocean. Some of it gets heated by the hot mantle underneath and melts a little. It is buoyant and rises. This is solid state convection with a "solid-fluid" that is somewhat less viscous than the mantle but a lot more viscous than melt. Blocks of the base of the solid crust founder as at ridge axes. In this regime the basalt is fluid enough

[7] If heat flow in plate tectonics is constant, the mantle reached a peak temperature at 2.7 Ga.

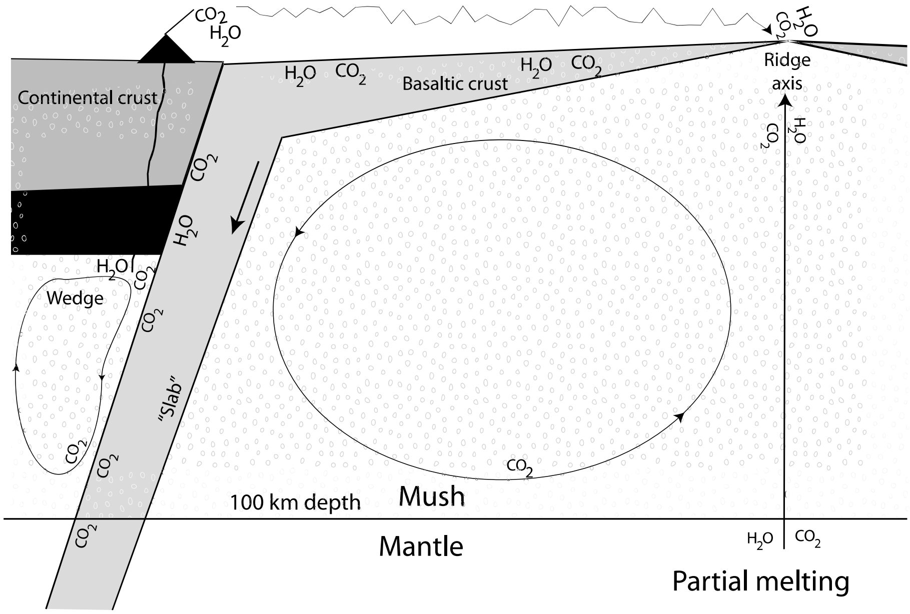

Fig. 11 Cartoon of crustal cycling in the Hadean. A basalt mush ocean sits atop the solid mantle. Heat flow is determined by convection in the solid mantle. The less viscous basalt does not substantially impede heat flow. The basalt ocean spreads and subducts much like the modern oceanic lithosphere. The basalt ocean is fed by partial melting of the underlying mantle and drained by subsidence into the mantle, the latter enabled by the phase change to garnet that occurs at a depth of ∼100 km (after Sleep 2007)

that the bottleneck on heat flow is set by solid state convection of the underlying mantle. The viscosity dependence of the upper mantle provides the thermostat. The basalt is fed by partial melting of the mantle and is drained by subduction of solid sinking slabs. The overall behavior of the basalt—upwelling at ridges and sinking of slabs—resembles plate tectonics, especially at the surface, but global heat flow does not depend upon subduction.

Impact churning of the seafloor suggests that Hadean basalts would be more deeply and thoroughly hydrated than their modern analogs. Upon sinking the basalts would be heated and the resulting hydrous melts would erupt as granitic rocks. These would be much more voluminous than now both because the extent of hydration was greater and because the speed of the recycling was greater. Kamber et al. (2005) emphasized that early "granites" would carry such a high abundance of radioactive elements that they would melt themselves if thick or deeply buried, which implies that early granites would tend to segregate themselves to the surface.

Neither heat flow nor the interior temperature need have decreased monotonically with time (Sleep 2000; Stevenson 2003; van Thienen et al. 2007, this issue). The surface heat flow as a function of mantle temperature may be multivalued, with a high heat flow from a mush ocean and relatively low heat flow for plate tectonics. It is possible that the lowest heat flow achievable with a mush ocean exceeds the highest heat flow achievable in plate tectonics, in which case the system either overcooled or alternated between regimes. Relatively brief episodes of mush ocean might have been key periods of rapid continent generation.

6.1 Zircons

The chief source of terrestrial data for the Hadean are ancient detrital zircons found in Archean and Proterozoic quartzites in the Jack Hills of Western Australia (Amelin et al. 2000; Wilde et al. 2001; Mojzsis et al. 2001; Valley et al. 2002; Cavosie et al. 2004; Cavosie et al. 2004; Harrison et al. 2005; Valley et al. 2005). Zircons are $ZrSiO_4$ crystals that are renowned for their durability. Zircon crystals readily incorporate uranium and hafnium. U–Pb dating gives accurate ages that can be as old as 4.4 Ga. The old zircons resemble those from modern granites (sensu latu) (Cavosie et al. 2004 and references therein). In particular, some of the granites apparently formed at the expense of sediments derived from meteoric weathering. Oxygen isotopes in ancient zircons provide compelling evidence that rocks on Earth were being chemically altered by liquid water before 4.2 Ga and probably before 4.3 Ga (Wilde et al. 2001; Mojzsis et al. 2001; Valley et al. 2002; Cavosie et al. 2005). The zircons are silent on whether the water was 273 K or 500 K, but they suggest that Earth's oceans were in place by 4.2 Ga.

Radiogenic Hf in 4.01 to 4.37 Ga zircons suggests that Lu, a more incompatible element than Hf and therefore quicker to segregate into a granitic crust, was already separating from Hf at 4.5 Ga (Amelin et al. 2000; Harrison et al. 2005). This result is somewhat controversial because interpreting the hafnium depends on the age of the zircon, but old zircons typically have many ages, and the hafnium is harvested from volumes that are large enough to sample several different ages. Nevertheless the least radiogenic hafnium demands separation before 4.4 Ga. Overall, the Lu–Hf data suggest that continents of a sort were already a significant presence on Earth's surface within a hundred million years of the Moon-forming impact. Segregation may even imply subaerial weathering in order to separate Lu from Hf in the sediments from which zircons were forged.

The existence of old zircons implies that there were places near the surface where zircons could be protected from subduction for hundreds of millions of years. Cavosie et al. (2004) presented a constraint on the vigor of crustal recycling processes after 4.4 Ga. Age gaps and clusters exist within their sample suite, just like with a modern orogenic belt. If further sampling confirms this finding, terrane-scale regions experienced tens of million year periods of quiescence. The age gaps between 4.4 and 3.8 Ga are 50–100 m.y., compared with 500–1000 m.y. for the subsequent history, including modern zircon suites. Taken at face value, this implies that crustal recycling rates were $\sim$10 times what they are now. The corresponding heat flow was $\sim$3 times the present, or 0.2 W/m^2. This cooling rate is consistent with those shown in Fig. 8. The lithosphere would have been 40 km thick, enough like the modern Earth to show plate-like characteristics. In any case, tectonics after 4.4 Ga were sluggish enough that some Hadean continental crust survived to at least the end of the Archean.

As a counterbalance to the natural tendency to over-interpret the zircons, we should not forget that until now ancient detrital zircons have been found in only one place on Earth. There is no guarantee that this one occurrence is representative, or that ancient continents were more than a local anomaly.

It is sometimes suggested that the impacts of the late bombardment are the reason why there are so few Hadean rocks, but if so the mechanism was probably indirect. First, both the Moon and Mars retain ancient surfaces despite impacts. Second, the expected (i.e., most probable) total energy released by late Hadean impacts on Earth would have been on the order of 10^{29} J, an order of magnitude less than the total geothermal energy over the same interval. Basic thermodynamics suggest that the geothermal forces did more work (Stevenson 1983). Cavosie et al. (2004) found no evidence of impacts in their sample of detrital zircons going back to $\sim$4.4 Ga. This includes zircons with metamorphic rims, which might show annealed shock features. On the other hand, impact statistics are described by power laws in which much of the energy is concentrated in the single largest event. If this event was itself extreme (we are deep in the realm of small number statistics here), then we could imagine the whole rock record erased by a single impact, with an estimated likelihood on the order of 10% (such an impact would vaporize the oceans and melt much of the exposed crust). The greater likelihood is that impacts played a major role in preparing early continental material for subduction, but it was Earth itself that erased its history.

6.2 Continental Crust

The debate about the timing of crustal growth rumbles quietly on. In the 1970s and 1980s Armstrong (1981) challenged the widely held belief that continental crust has grown continuously and that little crust existed before about 3.8 Ga. He suggested that the crust had reached its present volume by the end of the Hadean and that recycling has counterbalanced growth ever since. Since then some geochemists continue to argue for crustal growth (e.g. Coltice et al. 2000), but several factors have tilted the balance Armstrong's way. Widespread discoveries of ultrahigh pressure metamorphism (Coleman and Wang 2005) and seismic-tectonic evidence of subduction of lower continental crust in the Himalayas have provided a credible mechanism of crustal recycling (von Huene and Scholl 1991; Jahn et al. 1999; Elburg et al. 2004). Relicts of very old continental crust continue to be found in all Archean cratons. The outcrops of 4 Ga Acasta gneiss total at most a few square kilometers and represent only a minute fraction of the original Acasta continent: the rest was lost by recycling or reworking. And the Mt. Narryer zircons record the existence of Hadean continents from which no rock remains; yet the survival of these zircons for a billion years at the surface of the unstable Hadean Earth requires the persistence of a stable platform which can only have been continental lithosphere.

6.3 Ocean Volume and Depth

Many Archean volcanic rocks appear to have erupted under water onto a continental substrate. At Kambalda in Australia, for example, pillow basalts (which indicates underwater eruption) contain old zircons and geochemical signatures that record assimilation of old continental crust; and the Belingwe belt in Zimbabwe is made up of a shallow- to deep-water sequence of volcanic and sedimentary rocks that unconformably overlies an older granitic basement. It seems that at the time these rocks formed during the late Archean, oceans flooded much of the continental crust.

The simplest explanation is that the volume of the oceans was greater. Earlier we described how hydrogen is lost to space decreasing the Earth's water content. The total amount of water was greater in the Hadean than at present. But the volume of the oceans depends also on the partitioning of the water between the surface and the mantle and this depends on mantle temperatures. At present water and other volatiles migrate to the surface in partial melts and are returned to the mantle in subducting plates. Much of the altered oceanic crust that contains the water dehydrates at shallow depth. Most of the water escapes to the surface in subduction-related magmas and only a small fraction penetrates deeper. The dehydration reactions are temperature dependant and the plate is stripped of water shallower and more efficiently when the mantle is hotter. If the mantle cooled progressively though Earth history, the ocean volume should have progressively declined; while if the mantle hit a maximum temperature in the mid to late Archean (Sleep 2000), the proportion of water at the surface should also have been greatest during the mid to late Archean.

7 Hadean Atmosphere and Climate

Hades can also suggest icy wastes trapped in perpetual winter. It is not as certain that Earth was at times bitterly cold as it is certain that Earth was once infernally hot, but the argument that a lifeless young Earth should have been very cold when not very hot is good. The key point is that the young Sun was much fainter than it is now (Fig. 1). If a snowball Earth seems plausible in the Neoproterozoic, when the Sun was 96% as bright as it is now, it should seem more plausible when the Sun was just 71% as bright as it is now. A warm Hadean Earth needs either enormous geothermal heat flow or abundant greenhouse gases. As discussed earlier, geothermal heat was comparable to insolation during accretion, and at times much bigger, but its role was confined to aftermaths of big collisions. Geothermal heat was probably climatologically insignificant after 4.5 Ga. Of greenhouse gases the only good candidates are CO_2 and CH_4[8]. Methane can help provided that there are reducing agents and catalysts to generate it from CO_2 and H_2O. On Earth today methane is mostly made by biology. Methane is a good candidate for keeping Earth warm once it teemed with life, but it is not clear what the catalysts for making it would be when Earth was lifeless (Shock et al. 2000).

That leaves CO_2. It takes about a bar of CO_2 in the atmosphere to provide enough greenhouse warming to stabilize liquid water at the surface (Fig. 10). Although this is only about 0.5% of Earth's carbon inventory, it is 3,000 times more than is there today. CO_2 would have been scoured from the Hadean oceans by chemical reactions with abundant ultramafic volcanics and impact ejecta to make carbonate rocks (Koster van Groos 1988; Zahnle and Sleep 2002). The relatively fast time scales governing the early Hadean CO_2 cycle suggest that oceanic CO_2 was controlled by a fast crust–mantle cycle. The first question is whether carbonates were subducted into the mantle. If they were, the CO_2 atmosphere would have been thin and the surface very cold. If not, and if there were no continents on which to store carbonate rocks, the CO_2 would have remained in the atmosphere (Sleep et al. 2001) and the surface would have approached 500 K (Fig. 10). Sleep et al. (2001) did not identify a mechanism to sustain CO_2 at the intermediate $\sim$1 bar level needed to maintain a clement climate, which is not to claim that such a mechanism does not exist.

7.1 Ice

Ice thickness on a snowball Earth is a matter of active debate (McKay 2000; Warren et al. 2002; Pierrehumbert 2004; McKay 2004; Pollard and Kasting 2005). Thick ice solutions occur when the ice is white and opaque, full of bubbles and flaws. In a thick ice solution, ice thickness is determined by thermal conduction of geothermal heat. At a Hadean heat flow of 0.3 W/m^2, the ice would be 300 m thick. Thin ice solutions occur near the equator if the ice is transparent (black ice). In a thin ice solution, ice thickness is determined by thermal conduction of sunlight transmitted through the ice. Thin ice is predicted to be 1–5 m thick and easily broken up by winds. Using standard algorithms for sea ice, Pollard and Kasting estimated that a thin ice solution would typically present 2% open water. This is more than enough to permit efficient gas exchange between the atmosphere and ocean (Sleep and Zahnle 2001). Available evidence suggests that sea ice freezes as black ice if it freezes slowly (McKay 2004; Pollard and Kasting 2005).

[8] Water vapor is in fact the most important greenhouse gas, but it is a dependent variable, mobilized from oceans and ice sheets as needed.

The chief data-based argument favoring thick ice stems from a particular theory for how the cap carbonates formed. The NeoProterozoic snowball Earth events end with several-meter-thick carbonate beds of anomalous isotopic composition. The cap carbonates can be explained as volcanic CO_2 that had accumulated in the atmosphere to levels great enough to melt the ice (Pierrehumbert 2004). The chief data-based argument that the ice was thin is that the evolutionary record of life on Earth seems unaffected by the Neoproterozoic snowball events (Knoll 2003), which is surprising given that an ice shell thick enough to segregate oceanic and atmospheric CO_2 reservoirs would also be thick enough to extinguish most photosynthetic organisms[9].

In the Hadean, the fainter Sun favors thick ice, while Earth's faster rotation and generally higher heat flows favor thin ice. For an early Hadean heat flow of 1 W/m^2, the thick ice solution would be only 100 m thick. Even when the average heat flow was 0.3 W/m^2, heat flow would not have been the same everywhere, and we might reasonably expect substantial areas with heat flows in the range of 1 to 10 W/m^2, thinning the thick ice to 10–100 m. Io provides some guidance here. Much of Io's heat flow is concentrated in a few hot spots. The biggest volcano generates $\sim 1.2 \times 10^{13}$ W (Spencer et al. 2000). This one volcano accounts for 15% of the global heat flow. The heat flow around it is equivalent to 10 W/m^2 over an area 1,000 km across. A heat flow of 10 W/m^2 implies that even the thick ice solution would be only 10 m thick. Thin ice solutions, which depend on diffusion of sunlight through the ice, are independent of heat flow once established, but obviously could be triggered by high local heat flow.

As the global heat flow declined the prospects for thick ice improved. One can imagine a thermostatic negative feedback, roughly analogous to the stabilizing negative feedback we posited for water over an ocean of magma, in this case operating between atmospheric greenhouse gases and the surface areas covered by thin and thick ice (Pollard and Kasting 2005). In this feedback volcanic CO_2 would build up to the point where there are enough regions of thin ice near the equator to permit adequate ocean-air gas exchange. The ocean crust would provide the sink on CO_2.

7.2 Doubts

Our cold early Earth is a product of pure reason. We start from the best established datum—the faint Sun—and conclude that the Hadean ought to have been cold provided that the seafloor consumed CO_2. But in fact the temperature of the Archean, and by extrapolation of the Hadean, is a topic of vigorous debate. The major sources of data are inferred weathering rates and oxygen isotopes. Proponents of a cool Archean cite evidence that Archean weathering rates were not markedly different from today's (Holland 1984; Condie et al. 2001; Sleep and Hessler 2006), while proponents of a hot Archean make similar arguments for their side (Schwartzman 2002). Weathering rates depend on many things including temperature; there does not yet appear to be anything approaching a consensus.

The oxygen isotopes are more directly interpreted as a thermometer. Presumptively ocean-deposited carbonates and silicates show a progressive increase in oxygen isotopic fractionation over the history of the Earth. This can be interpreted as a change of seawater composition (traced to changing temperatures of rock-water interactions), as a product of diagenesis (the older samples are on average more cooked), or as a direct measure of

[9] Plausible refugia in hot springs or in endolithic communities on islands or continents make complete extinction unlikely (Kirschvink 1992).

decreasing seawater temperatures (so that the precipitates become increasingly more fractionated with time). If the latter, the mid-Archean oceans would have been ~340 K (Knauth and Lowe 2003). Such high temperatures require a potent greenhouse effect. Three bars of CO_2 would be needed (less if supplemented by a lot of CH_4).

This sort of atmosphere is most likely if (1) the seafloor sink was insignificant (so that continental weathering was the main CO_2 sink); (2) emergent continents were few (to shrink the sink); and (3) biology has always been an important catalyst of chemical reactions between CO_2 and continental rocks (Schwartzman 2002). By presumption the catalytic weathering powers of biology have improved as life evolved. In this picture the history of atmospheric CO_2 presents an inverted image of the history of biological evolution (*ibid*). These arguments imply that the Hadean would also have been hot if the Hadean seafloor was not a significant sink of CO_2.

8 The Late Bombardment

A major scientific result of the Apollo program is that the Moon was hit by several 100-km-size asteroids and by hundreds of 10-km-size asteroids ca. 3.9 Ga (Wilhelms 1987). Earth was hit at the same time, and because Earth's effective cross section is 20 times bigger than the Moon's, Earth was hit 20 times as often. Not only was Earth hit by a hundred 100-km asteroids (or comets), it was also hit by a dozen bodies bigger than any to hit the Moon. Here we speak of probabilities in lieu of direct evidence, but the biggest asteroid likely to hit the Earth ca. 3.9 Ga would have been comparable to Vesta or Pallas; that is, as big as any asteroid now in the asteroid belt. Whether these impacts were the tail end of a sustained bombardment dating back to the accretion of the planets or whether they record a catastrophe associated with a rearrangement of the architecture of the solar system (e.g. Gomes et al. 2005) is contentious but obviously of some importance to the Hadean environment.

8.1 The Lunar Record

Debate over the lunar cratering record has tended to emphasize two extreme views. Hartmann et al. (2000) and Ryder et al. (2000) provided recent reviews written from the perspectives of active participants in this debate, while Chyba (1991) and Bogard (1995) provided careful reviews written from more centrist perspectives. Different conceptions of the lunar cratering record are illustrated in Fig. 12.

At one end, Hartmann (1975) and Wilhelms (1987) presumed that the observed basins and craters mark the end of a monotonically declining impact flux that extrapolates smoothly back in time to the origin of the Moon. Such enormous hidden impact fluxes present serious challenges. There isn't enough contamination of the lunar crust by extreme siderophiles (elements such as iridium that partition strongly into the core) that would have been abundant in the impacting bodies (Sleep et al. 1989; Chyba 1991; Ryder 2003), and the ancient anorthositic crust has not been obliterated, as would be the case if the Moon were saturated with Imbrium-sized basins (Baldwin 1987a, 1987b). Mars too shows little evidence of a hidden history of catastrophic cryptic craters. The preservation of a 4.5 Ga martian rock—the famous martian meteorite ALH84001, which was found in Antarctica—is inconsistent with the ancient Martian surface being pulverized into oblivion. And how did the differentiated asteroid Vesta survive with its basaltic crust intact? Moreover, it is difficult to point to any otherwise inexplicable data that might be explained by extremely high impact fluxes predating the observable crater record.

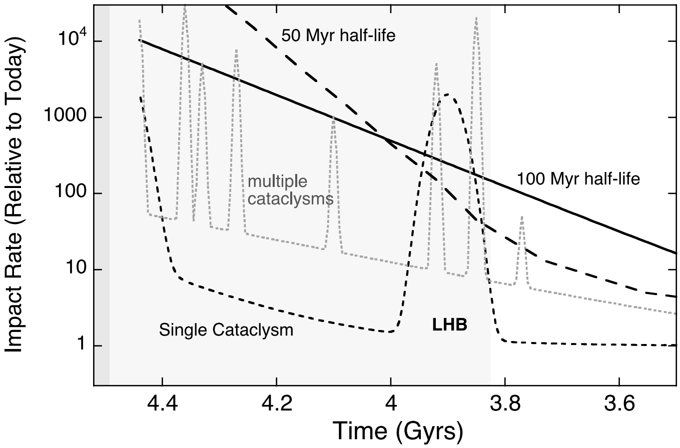

Fig. 12 Four concepts of the late lunar bombardment. The "100 Myr half-life" is Neukum's standard lunar crater curve for times after 3.86 Ga. It is calibrated to crater counts and surface ages from Apollo landing sites and the Imbrium impact basin (Neukum and Ivanov 1994; Neukum et al. 2001). The steeper "50 Myr half-life" extrapolation uses the same data but it also uses the young 3.92 Ga age for the Nectaris impact basin and crater densities on still older but undated surfaces (after Wilhelms 1987). The "single cataclysm" is a schematic but quantitatively representative late cataclysm as advocated by Graham Ryder (2002, 2003). "Multiple cataclysms" scatters several cataclysms over the Hadean (Tera et al. 1974). Available data do not favor the more aggressive 50 Myr half-life before 4.0 Ga. The terrestrial and Vestan impact records favor the higher standard impact rates ca. 3.2–3.5 Ga

The other extreme view is that the late lunar bombardment was an actual event confined to a relatively short period of time. This hypothetical event was named the "late lunar cataclysm" by Tera et al. (1974). The late lunar cataclysm remains an important and testable hypothesis. In its most extreme form, Ryder (2002, 2003) limited the total lunar impact record to just those craters and basins that survive today, and he stuffed them all into a 50–100 Myr window ca. 3.9 Ga. In Ryder's view, impacts may have been as infrequent before 3.95 Ga as they are now.

Both extreme points of view are represented on Fig. 12. Although a cartoon, the figure is quantitatively faithful. The cataclysm is shown either as a single event (Ryder) or as several events (Tera et al. 1974). Also shown on the Fig. 12 is Neukum's "standard" lunar cratering history, which is in wide use in discussions of inner solar system chronometry (Neukum and Ivanov 1994).

There is some evidence that sides with the cataclysm. Tera et al. (1974) gave several arguments, the most durable of which is lead-based. Taylor (1993, p. 172) gave an updated version with shortened error bars. The argument is that a ^{207}Pb–^{206}Pb plot for lunar highland breccias gives a straight line—a mixing line between end-members at $\sim$4.46 Ga and $\sim$3.86 Ga—that is distinct from the curved concordia that one would see if all intermediate ages were represented. Tera et al. interpreted this as evidence for a lead mobilization event ca. 3.9 Ga, which they attributed to impact shock metamorphism.

Lunar basins Imbrium (3.85), Serenitatis (3.89), Crisium (3.91), and Nectaris (3.92) have been independently dated (see Ryder et al. 2000) and, if these dates are correct, clearly cluster around 3.9 Ga. Crater densities superposed on the ejecta blankets from these basins imply that ca. 3.85 Ga the impact flux decayed with a half-life of $\sim$50 Myr. The four big nearside basins also provide an obvious source of $\sim$3.9 Ga impact metamorphosed nearside highlands rocks. Whether farside lunar breccias share this common age is unknown.

Histograms of Apollo data suggest an impact spike but don't demand it (Wetherill 1975; Bogard 1995). An alternative to a cataclysm is to argue that the Imbrium impact reset all the radiometric clocks (Haskins 1998). Another alternative chronology dates Imbrium at 3.77 Ga (Stadermann et al. 1991), a blasphemy that Ryder rejected without comment.

Cohen et al. (2000) avoided Apollo sampling biases by using lunar meteorites recovered in Antarctica. They found a scattering of dates, none older than about 3.9 Ga. They argued that the distribution of ages supports a cataclysm at 3.9 Ga. However, using Antarctic meteorites introduces a different bias, one that favors strong competent target surfaces (Melosh 1989; Warren et al. 1989; Gladman 1997). All but one of the meteorites from Mars were ejected from young basalts—clearly a biased sample. Lunar meteorites are much smaller and no more numerous than martian meteorites. The straightforward story is that it is difficult to eject rocks from the Moon into space by impact because strong rocks are rare near the surface, and it is more difficult to launch old rocks because old strong rocks are even more rare.

8.2 Other Sources of Data

The asteroid Vesta is a $\sim$500 km diameter fully differentiated world (core, mantle, basaltic crust) that resembles a miniature terrestrial planet. It is located near the inner edge of the asteroid belt and is a significant source of meteorites. These meteorites carry a record of strong shock events that correspond to the late bombardment of Vesta. These shock ages are spread between 3.4 and 4.1 Ga (Bogard 1995). The record at Vesta seems inconsistent with an inner-solar-system-wide late cataclysm.

The Archean Earth also retains evidence that big impacts were still relatively frequent as late as 3.2 Ga (Lowe and Byerly 1986; Lowe et al. 1989; Byerly et al. 2002; Kyte et al. 2003). The evidence takes the form of spherule beds, which from their siderophile element abundances were almost certainly impact generated. There were at least four of these events between 3.2 and 3.5 Ga. The extant spherule beds are all much thicker than those left behind by the K/T impact. To the extent that one can extrapolate worldwide catastrophes from a small number of samples, all four appear to have been bigger than the K/T event. Extrapolation suggests that the thickest spherule bed corresponds to an impact on Earth 50–300 times bigger than the K/T (Kyte et al. 2003), making it as big as the Imbrium impact on the Moon. Such an impact is big enough to boil off 40 meters of ocean water. To our knowledge there is no evidence of such a catastrophe, although the geologic record of the time is scanty and controversy surrounds even the most basic issues.

8.3 Theorists Prefer Cataclysms

Öpik–Arnold simulations of orbital evolution suggested that the characteristic time scale for sweep up of stray debris in the inner solar system was some $\sim$100–200 Ma years (Wetherill 1975). This result implied that a monotonic decline in the impact rate was easy to explain, but cataclysm required something special. Wetherill (1975) showed that collisional disruption of a Vesta-sized asteroid is a 10^{11} year event in the current solar system, which makes a collisional source of the late bombardment a $\sim$1% chance event. Wetherill suggested that tidal disruption of a Vesta-sized body passing Earth is more likely.

Öpik–Arnold simulations use Monte Carlo techniques to perform otherwise impractical computations. When more powerful computers made direct numerical integrations possible, it was found that Öpik–Arnold methods greatly underestimate the chance that a stray body hits the Sun. The longest-lived inner solar system reservoir has only a $\sim$40 Myr half-life

(Morbidelli et al. 2002). This is too short to explain a monotonic impact history. A suitable longer-lived source of more distant asteroids in unstable orbits has yet to be identified, although there may be reasonable candidates in the outer asteroid belt or beyond that haven't been fully studied.

There are a lot of dynamical theories that can explain a spike in the impact rate. In general these posit a rearrangement of the architecture of the solar system taking place ca. 3.95 Ga. A good recent example is a series of papers by Gomes et al. (2005) that posit Saturn and Jupiter evolving through the 2 : 1 resonance[10]. Another story posits Uranus and Neptune forming between Saturn and Jupiter, with both being scattered out to their present locations (Thommes et al. 2002). A third possibility is that a small planet in the asteroid belt was ejected by Jupiter after a suitable interval, producing a rain of asteroids (Chambers and Lissauer 2002).

In the theories the rearrangement itself is a brief event, and precisely when it occurs is up to the discretion of the modelers, although a time scale of hundreds of millions of years is physically plausible. The key consequence of rearranging the planets for the late bombardment is that Jupiter moves, and when Jupiter moves, the resonances that disturb the asteroid belt move with it. The net effect of moving major resonances into a previously stable part of the asteroid belt is to unleash an asteroid shower onto the inner solar system (Levison et al. 2001). The natural time scale of the asteroid shower is some 20–100 million years (Levison et al. 2001). The magnitude of the asteroid shower depends on the mass of the primordial asteroid belt near important resonances, but is plausibly that of the lunar late bombardment.

It is also probable that moving the planets triggers a comet shower into the inner solar system (Levison et al. 2001). The comet shower is brief, lasting some 10–20 Myr (Levison et al. 2001). In these theories Uranus and Neptune come to rest by landing in a thick primordial belt of planetesimals. The magnitude of the comet shower is estimated by multiplying the presumed mass of the belt (30 Earth masses) by the probability that a stray body in the vicinity of Uranus or Neptune will hit the Moon ($\sim 10^{-8}$, Levison et al. 2001). The predicted comet flux of 2×10^{18} kg is about a tenth of the inferred mass of the lunar LHB (Chyba 1991; Ryder 2002; Zahnle and Sleep 2006), which is close enough to be interesting, but two orders of magnitude short of what it is needed to give Earth its oceans.

On balance, we prefer cataclysms over monotonic decay. To our minds the most telling argument against a huge unseen Hadean impact flux is that it doesn't explain anything else in the solar system that needs explaining; it's a kind of dead end. By contrast, a cataclysm (or cataclysms) fits in well with current concepts of how a solar system might evolve. Mechanisms devised to generate a cataclysm have suggested explanations for other unexplained solar system properties. Background impact rates before a cataclysm would have been much higher than they were afterward, because there were vastly more stray bodies in the solar system before the cataclysm cleared them away. An issue is that the impact rate after 3.9 Ga decays more slowly than theory predicts. In our opinion this failure is better attributed to incompleteness in the theory than to a fundamental flaw.

[10]The idea is that Saturn was formed closer to the Sun and evolved outward. When Saturn's year was twice Jupiter's year (2 : 1), the resonance between their orbits caused havoc that launched showers of asteroids and comets into the inner solar system while quickly driving Saturn further from the Sun. The theory explains several traits of the solar system.

8.4 Transient Environmental Effects of Impacts

Today, the total number of prokaryotes on Earth is estimated to be 4–6 $\times 10^{30}$ cells (Whitman et al. 1998). The nature of the first micro-organisms on Earth and how they survived the early conditions on Earth is necessarily a matter of some conjecture, but asteroid and comet impacts must have played an important role in the emergence of life and its prebiotic precursors.

The evidence of heavy bombardment in the Hadean suggests that impact events played a role in defining the physical characteristics of the early Earth, and thus the physiological traits of organisms that would have been required to colonize ecological niches periodically subjected to these events. The emergence of life, or at least the isotopic evidence for its presence, occurs soon after the period of late bombardment (e.g., Schidlowski 1988), suggesting that prebiotic or biological processes were ongoing during bombardment and radiated rapidly as the impact flux declined.

Impactors larger than 500 km could have boiled the entire ocean. Based on the statistical properties of lunar basin-forming impactors, we expect some zero to four impacts big enough to evaporate the oceans and heat the surface to the melting point (Fig. 13) between the time of the formation of the Earth and $\sim$3.8 Ga ago. In such events life evolving in the oceans may have been extirpated (Sleep et al. 1989; Zahnle and Sleep 1997). These events may have favored life in the deep regions of the Earth below the oceans. Russell and Arndt suggested that prebiotic evolution in hydrothermal vents would have created acetogenic precursors to life, which may have migrated into the ocean floor. The presence of these precursors in the ocean floor would have allowed for the evolution of life in environments protected from impacts (Russell and Arndt 2005).

The occasional boiling of the oceans provides a compelling explanation for the hyperthermophilic root of the phylogenetic "tree of life" (Pace et al. 1986; Lake 1988; Maher and Stevenson 1988; Sleep et al. 1989). Of course, the hyperthermophilic root of life does not suggest that life originated in hot conditions, nor does the first organism need to have been a hyperthermophile; the tree of life merely suggests a bottleneck resulted in the survival of hyperthermophiles that led to the diversity of life on Earth today. Impact events, by periodically boiling the oceans and providing a globally distributed source of heat, may have caused this bottleneck. But if life did originate and evolve to something like its current complexity in hydrothermal systems at the bottoms of oceans, life should be widespread in our solar system, independently evolving wherever one finds hydrothermal systems charged with simple C- and N-containing molecules. Several icy moons meet or have met these criteria; many of the larger asteroids, comets, and Kuiper Belt Objects have met them too. Hydrothermal origin of life is therefore a testable hypothesis.

It is not clear that, even if early impactors had extirpated the entire biosphere by boiling away the oceans and heating the early crust, life would have been completely reset. Impacts can lift surface rocks into orbit essentially unshocked and unheated (Melosh 1989). Going into orbit might be viable strategy (Sleep and Zahnle 1998; Mileikowsky et al. 2000; Wells et al. 2003). Modeling results suggests that life could have been launched in rocks into space, to return to the Earth several thousand years later and reseed the planet (Wells et al. 2003). Wells's data suggest that with an initial cell population of 10^3–10^5 cells/kg, at least one cell in this material would return after 3,000–5,000 years following a sterilizing impact. Qualitatively similar conclusions have recently been obtained by Gladman et al. (2005) who showed that 1% of the impact ejected material might eventually return to Earth.

Recent experiments on the shock survival of the microorganisms, *Bacillus subtilis* and *Rhodococcus erythropolis* suggest that they can survive high shock pressures (up to 78 GPa)

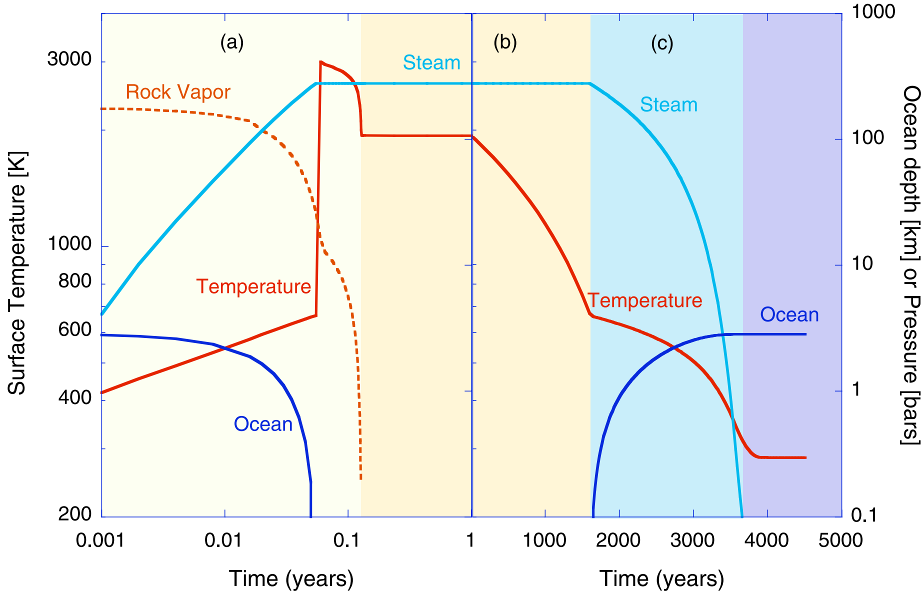

Fig. 13 History of an ocean vaporizing impact. (*a*) The impact produces 100 bars of rock vapor. Somewhat more than half the energy initially present in the rock vapor is spent boiling water off the surface of the ocean, the rest is radiated to space at an effective temperature of ~2300 K. (*b*) Once the rock vapor has condensed the steam cools and forms clouds. Thereafter cool cloudtops ensure that Earth cools no faster than the runaway greenhouse threshold, with an effective radiating temperature of 270 K. (*c*) The steam atmosphere becomes cool enough for rain to reach the surface. Some examples of what happens after smaller impacts on Earth are shown in the chapter by Nisbet et al. (2007, this issue).

associated with launch from a planetary surface (Burchell et al. 2004). The low temperatures inferred from the mineralogy of the interior of meteorites from Mars (Weiss et al. 2000) also suggest that meteorites can re-enter the Earth's atmosphere while maintaining internal temperatures low enough to preserve viable organisms. Depending on how long they remain in space and the degree to which their DNA is damaged by radiation exposure, it seems that escape from Hadean impacts and later return to Earth is plausible.

After about 3.8 Ga, impact events would have had effects confined to boiling of the surface layers of the oceans. The boiling of the surface layers has been suggested to have delayed the evolution of photosynthesis since a sufficient flux of light for this mode of metabolism requires living in the top ~200 m of the oceans. Maher and Stevenson (1988) also pointed out that episodic darkness caused by the injection of dust and rock into the atmosphere would have been inhibitory to photosynthesis by blocking a source of light. These events need not have prevented the establishment of photosynthesis, however.

Smaller impacts are less potent but there would have been hundreds capable of melting oceanic ice sheets. Each big impact triggers a brief impact summer. Impacts big enough to melt the ice occurred on a ~1 Myr time scale (Fig. 14).

The other potentially life-changing aspect of late impacts is their power to drive chemistry (Kasting 1989). An obvious agent of change would have been the big iron asteroid. These exist; indeed they were probably rather plentiful. Chemical reactions of H_2O and CO_2 with iron can generate considerable amounts of reduced gases, H_2 and CH_4 in particular. Methane is both a greenhouse gas and a desirable starting point for prebiotic chemistry.

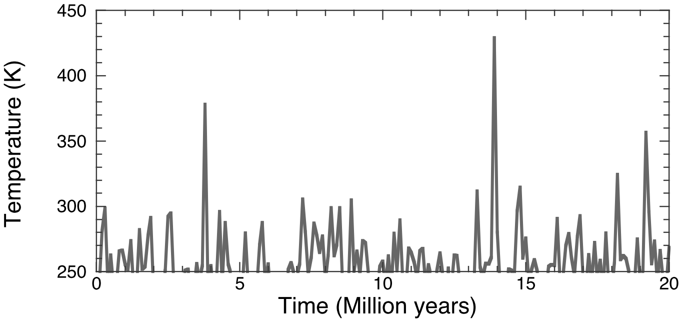

Fig. 14 An exemplary Monte Carlo slice of the Hadean during the LHB. Big impacts occasionally melt the ice and create temporarily warm or even hot conditions. The figure shows the warmest events occurring over a random 20 million year interval; each point plotted is the warmest event in a 100,000 year interval

The aftermath of a big iron impact seems an especially auspicious time to try to generate life.

Hydrogen and methane are also generated by serpentinization of ultramafic impact ejecta. We estimated that ca. 3.85 Ga impact ejecta were mobilizing ferrous iron at an inconstant rate on the order of 10^{13} moles/yr (Zahnle and Sleep 2002). The generic serpentinization reaction is $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$, so that at 3.85 Ga the H_2 source might have been on the order of 3×10^{12} moles/yr (about an order of magnitude larger than the current source). In the aftermath of big impacts the H_2 source would have been at least an order of magnitude larger still and, especially when coupled with a similarly enhanced CH_4 source, would have had profound influence on atmospheric chemistry.

9 Conclusion

In this essay we first set the stage for the Earth, and then we track Earth through the Hadean. The general point of view is to bracket the Hadean Earth between boundary conditions. The Moon-forming impact provides the initial condition, while a smooth transition from the Hadean into the early and mid-Archean almost a billion years later provides the end point.

The embryos of the terrestrial planets formed quickly, perhaps less than 1 million years after the origin of the solar system. Fast formation implies that they captured primary nebular atmospheres. Evidence of primary atmospheres is preserved in the noble gases. The colder embryos also held indigenous stores of water ice or hydrous minerals made from melted ice. Collisions and mergers between the embryos built up a smaller number of larger ones, which by this point can be called planets. Much of this growth took place after the solar nebula was dispersed. Collisions between the planets and a generally corrosive environment outside the nebular cocoon caused the planets to lose volatiles as they evolved. Losses were most severe for the smaller planets and the planets nearest the Sun. These losses were offset for planets that accreted planets or embryos or stray bodies from the colder, more-distant reaches of the solar system, where condensed volatiles were more abundant. This picture provides plausible context for the collision between a Mars-sized planet that had lost its volatiles and a larger, Earth-sized planet that had held on to its own.

The Moon-forming impact took place some 40–50 Ma after the solar system formed. The aftermath left Earth enveloped in a hot silicate atmosphere. At this time Earth's effective radiating temperature—$\sim$2,500 K—was set by the optical depth of silicate condensates. Fast cooling at high temperature ensured that the silicate vapor atmosphere did not last long. The silicates would have condensed and receded into the depths of the planet within $\sim$1,000 yrs. Volatiles would have partitioned according to their solubility in silicate melt, with much of the H_2O partitioning into the mantle, while CO_2 and most other gases were left behind as a deep thick atmosphere.

Thereafter thermal blanketing by the atmosphere reduced the effective radiating temperature dramatically. The latter gradually approached the asymptotic $\sim$300 K radiating temperature of a water vapor atmosphere. The resulting cooling rate was orders of magnitude slower than for an airless planet with a magma surface. We estimate that, because of thermal blanketing, it took would have taken $\sim$2 Myrs for the surface of a magma ocean to freeze. During this time tidal heating by the new Moon was a major energy source in the mantle. But because the atmosphere controlled the rate of mantle cooling, thermal blanketing would have controlled the pace of lunar orbital evolution. The slow lunar orbital evolution that results can help explain how the Moon acquired its inclination.

Water was expelled from the mantle as the magma ocean froze. This generated a thick steam atmosphere. The steam atmosphere kept the surface near the melting point until the mantle dried out. Thereafter the mantle solidified and geothermal heat was no longer climatologically significant. Without the support of geothermal heat the steam condensed and rained out over a relatively short time, forming oceans of hot water. At this point the atmosphere was dominated by $\sim$100 bars of CO_2, and the surface temperature was $\sim$500 K. Further cooling was governed by how quickly CO_2 was removed from the atmosphere. Vigorous hydrothermal circulation through the oceanic crust and rapid mantle turnover could have removed 100 bars of CO_2 from the atmosphere in as little as 10 million years. However, the balance of the CO_2 cycle remains obscure, which makes it difficult to predict how quickly this would have happened and what the asymptotic atmospheric CO_2 level would be. If carbonate subduction were efficient, and its scavenging from the atmosphere and ocean promoted by abundant ultramafic crust and abundant impact ejecta, a lifeless Earth should have been cold and its oceans white with ice. But if carbonate subduction were inefficient, most of the CO_2 could have stayed in the atmosphere and kept surface temperatures near $\sim$500 K for many tens of millions of years. Intermediate states exist but require a finely tuned CO_2 cycle. Hydrous minerals entered the hot mantle less easily than carbonates, which suggests that the mantle was dry and Earth's water was mostly partitioned into oceans.

The transition between vigorous magma ocean convection and modern plate tectonics is unlikely to have been simple or direct. Plate tectonics as it works now has difficulties with heat flows much greater than 0.1 W/m^2 from a mantle distinctly warmer than it is now; it was probably inadequate to handle typical Hadean heat flows of 0.2–0.5 W/m^2. In place of plate tectonics we suggest that the mantle was topped by a $\sim$100 km deep basaltic mush that, unlike modern plates, was relatively permeable to heat flow. This picture resembles the idealized physics of parameterized convection, more so than plate tectonics does. Recycling and distillation of hydrous basalts produced granitic rocks very early, which is consistent with preserved $>$4 Ga detrital zircons.

Earth could have been habitable as early as 10–20 Myrs after the Moon-forming impact if CO_2 entered the mantle efficiently. But in the absence of potent greenhouse gases, the faint Sun suggests that the Hadean would not have enjoyed a stable, pleasant climate. Simple models suggest that the modest 1 bar CO_2 atmosphere needed to maintain a clement climate represents an unlikely balancing point for a lifeless planet: the simple models favor either too little CO_2 (efficient subduction) or too much (inefficient subduction). Of course these are just models; moreover the real world would have presented a range of subduction environments that might have averaged out just right. Nevertheless we take the view that a lifeless Hadean

Earth was likely ice-covered at most times and places, that the ice was thin near the equator or over regions of locally high heat flow, with the thin ice broken by lanes and patches of open water, and that major impacts induced hundreds or thousands of transient impact summers.

As we emphasized in the Introduction, the Hadean is not data rich. The only points of surety are that the impact that made the Moon melted and superheated the Earth; that some 700 million years later recognizably terran rocks began to leave a permanent record of their existence; and that some zircons forged in the knowledge of liquid water found refuge there, so that today they can tell their tale. The rest of it is variously informed speculation intended as a framework (or foil) for further work. A few topics stand out. One is the importance of tidal heating to the thermal and perhaps the compositional evolution of the mantle as the magma ocean froze. Another topic is the mechanism of mantle convection between the freezing of the magma ocean and the onset of plate tectonics. A possibly related topic is how continents formed (or did not form) under these conditions. What was the clock that inserted a $\sim$30 Myr time delay between the Hf–W and U–Pb dating systems? Was it related to tectonic style or continent formation? Did the cooling mantle generate persistent slag layers and dregs layers at the top and bottom of the mantle? Did the Earth long maintain an ultramafic crust? Another general topic is how fast carbon dioxide was removed from the atmosphere into the mantle. This depends on the details of carbonate mineral stability as crustal blocks foundered into the mantle. It controls the evolution of the climate. Was there a feedback mechanism to provided the right amount of greenhouse warming to counter the faint Sun, or was the Hadean Earth really as cold and icy as we have surmised? These are just a few of the issues raised here. But the main goal for future research is simply to describe the full diversity of the Hadean surface and near surface environments. Until then we won't be close to an answer to the big question: just what was it about the Hadean that made it the Garden of Eden?

Acknowledgements We thank Yutaka Abe, Tom Ahrens, Luke Dones, Mikhail Gerasimkhov, Jim Kasting, Joe Kirschvink, Paul Knauth, Hal Levison, Jack Lissauer, Don Lowe, Chris McKay, Mark Marley, Steve Mojzcis, David Morrison, Bill Nelson, Francis Nimmo, Ian Parsons, Bob Pepin, David Schwartzman, John Spencer, and John Valley for discussions, insights, and explanations of thorny problems that for the most part they didn't realize would come to this. KZ thanks the NASA Exobiology Program, the NASA Planetary Geology and Geophysics Program, and the National Astrobiological Institute for support. NTA acknowledges the help of the French CNRS and the ArchEnviron program of the European Science Foundation. NS acknowledges support by NSF grant EAR-0406658.

References

Y. Abe, Proc. 21st ISAS Lun. Planet Symp. (1988), pp. 225–231

Y. Abe, Lithos **30**, 223–235 (1993)

Y. Abe, T. Matsui, J. Atm. Sci. **45**, 3081–3101 (1988)

Y. Abe, E. Ohtani, T. Okuchi, K. Righter, M. Drake, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (University of Arizona Press, Tucson, 2000), pp. 413–433

F.C. Adams, G. Laughlin, Icarus **150**, 151–162 (2001)

F.C. Adams, D. Hollenbach, G. Laughlin, U. Gorti, Astrophys. J. **611**, 360–379 (2004)

C.B. Agnor, W.R. Ward, Astrophys. J. **567**, 579–586 (2002)

C. Agnor, E. Asphaug, Astrophys. J. **613**, L157–L160 (2004)

T.J. Ahrens, J.D. O'Keefe, M.A. Lange, in *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. by S. Atreya, J.B. Pollack, M.S. Matthews (The University of Arizona Press, Tucson, 1989), pp. 328–385

C.J. Allégre, E. Lewin, Earth Planet. Sci. Lett. **96**, 61–88 (1989)

C.J. Allégre, E. Lewin, B. Dupré, Chem. Geol. **70**, 211–234 (1988)

Y. Amelin, D.-C. Lee, A.N. Halliday, Geochim. Cosmochim. Acta **64**, 4205–4225 (2000)
Y. Amelin, A.N. Krot, I.D. Hutcheon, A.A. Ulyanov, Science **297**, 1678–1683 (2002)
R.L. Armstrong, Phil. Trans. Roy. Soc., Lond. Ser. A **301**, 443–472 (1981)
D. Arnett, *Supernovae and Nucleosynthesis. An Investigation of the History of Matter, from the Big Bang to the Present* (Princeton University Press, Princeton, 1996)
E. Asphaug, C. Agnor, Q. Williams, Nature **439**, 155–160 (2006)
R.B. Baldwin, Icarus **71**, 1–18 (1987a)
R.B. Baldwin, Icarus **71**, 19–29 (1987b)
W. Benz, W.L. Slattery, A.G.W. Cameron, Icarus **66**, 515–535 (1986)
W. Benz, W.L. Slattery, A.G.W. Cameron, Icarus **74**, 516–528 (1988)
M. Bizzarro, J.A. Baker, H. Haack, Nature **431**, 275–278 (2004)
D.D. Bogard, Meteoritics **30**, 244–268 (1995)
A.P. Boss, in *Origin of the Earth*, ed. by H.E. Newsom, J.H. Jones (Oxford University Press, Oxford, 1990), pp. 3–15
S.A. Bowring, I.S. Williams, Contributions Mineral. Petrol. **134**, 3–16 (1999)
M. Boyet, R.W. Carlson, Science **309**, 576–581 (2005)
T.E. Bunch, S. Chang, Geochim. Cosmochim. Acta **44**, 1543–1577 (1980)
M.J. Burchell, J.R. Mann, A.W. Bunch, Mon. Not. Roy. Astron. Soc. **352**, 1273–1278 (2004)
G.R. Byerly, D.R. Lowe, J.L. Wooden, Science **297**, 1325–1327 (2002)
R.M. Canup, Icarus **168**, 433–456 (2004)
R.M. Canup, C.B. Agnor, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (Univ. of Arizona Press, Tucson, 2000)
R.M. Canup, E. Asphaug, Nature **421**, 708–712 (2001)
R.M. Canup, K. Righter, *Origin of Earth and Moon* (University of Arizona Press, Tucson, 2000)
A.J. Cavosie, S.A. Wilde, D. Liu, P.W. Weiblen, J.W. Valley, Precambr. Res. **135**, 251–279 (2004)
A.J. Cavosie, J.W. Valley, S.A. Wilde, E.I.M.F., Earth Planet Sci. Lett. **235**, 663–681 (2005)
J.E. Chambers, Earth Planet. Sci. Lett. **223**, 241–252 (2004)
J.E. Chambers, J.J. Lissauer, Lun. Planet. Sci. Conf. **33** (2002), abstract 1093
C.F. Chyba, Icarus **92**, 217–233 (1991)
C.F. Chyba, Geochim. Cosmochim. Acta **57**, 3351–3358 (1993)
P. Cloud, in *Earth's Earliest Biosphere*, ed. by J.W. Schopf (Princeton University Press, Princeton, 1983), pp. 14–31
P. Cloud, *Oasis in Space* (Norton, New York, 1988)
B.A. Cohen, T.D. Swindle, D.A. Kring, Science **290**, 1754–1756 (2000)
R.G. Coleman, X. Wang (eds.), *Ultrahigh Pressure Metamorphism* (Cambridge University Press, Cambridge, 2005)
N. Coltice, F. Albarède, P. Gillet, Science **288**, 845–847 (2000)
K.C. Condie, D.J. DesMarais, D. Abbott, Precambr. Res. **106**, 239–260 (2001)
J.N. Cuzzi, F.J. Ciesla, M.I. Petaev, A.N. Krot, E.R.D. Scott, S.J. Weidenschilling, in *Chondrites and the Protoplanetary Disk*, ed. by A.N. Krot, E.R.D. Scott, B. Reipurth. ASP Conference Series, vol. 341 (2005)
F. D'Antona, I. Mazzitelli, Astrophys. J. Suppl. **90**, 467–500 (1994)
G.F. Davies, J. Geophys. Res. **89**, 6017–6040 (1984)
R. Diehl et al., Nature **439**, 45–47 (2006)
B.R. Doe, R.E. Zartman, in *Geochemistry of Hydrothermal Ore Deposits*, ed. by H.L. Barnes (Wiley, New York, 1979), pp. 22–70.
M.A. Elburg, M.J. van Bergen, J.D. Foden, Geology **32**, 41–44 (2004)
C.N. Foley, M. Wadhwa, L.E. Borg, P.E. Janney, R. Hines, T.L. Grove, Geochim. Cosmochim. Acta **69**, 4557–4571 (2005)
S.J.G. Galer, S.L. Goldstein, Terra Abstr. **3**, 485–486 (1991)
H. Genda, Y. Abe, Icarus **164**, 149–162 (2003)
H. Genda, Y. Abe, Nature **433**, 842–844 (2005)
P. Goldreich, Rev. Geophys. **4**, 411–439 (1966)
R. Gomes, H.F. Levison, K. Tsiganis, A. Morbidelli, Nature **435**, 466–469 (2005)
B.J. Gladman, Icarus **130**, 228–246 (1997)
B.J. Gladman, L. Dones, H.F. Levison, J.A. Burns, Astrobiology **5**, 483–496 (2005)
A.N. Halliday, in *Meteorites, Comets and Planets*, ed. by A.M. Davis. Treatise on Geochemistry, vol. 1 (H.D. Holland and K.K. Turekian) (Elsevier-Pergamon, Oxford, 2003), pp. 509–557
A.N. Halliday, Nature **427**, 505–509 (2004)
A.N. Halliday, T. Kleine, in *Meteorites and the Early Solar System II*, ed. by D. Lauretta, L. Leshin, H. MacSween (Univ. of Arizona Press, 2006, in press)

C.L. Harper, S.B. Jakobsen, Science **273**, 1814–1818 (1996)
T.M. Harrison, J. Blichert-Toft, W. Müller, P. Holden, F. Albarede, S.J. Mojzsis, Science **310**, 1947–1950 (2005)
W.K. Hartmann, Icarus **24**, 181–187 (1975)
W.K. Hartmann, R.J. Phillips, G.J. Taylor (eds.), *Origin of the Moon* (Lunar and Planetary Institute, Houston, 1986)
W.K. Hartmann, L. Dones, G. Ryder, D. Grinspoon, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (University of Arizona Press, Tucson, 2000), pp. 493–512
L.A. Haskins, J. Geophys. Res. **103**, 1679 (1998)
C. Hayashi, K. Nakazawa, H. Mizuno, Earth Planet. Sci. Lett. **43**, 22–28 (1979)
H.D. Holland, *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, Princeton, 1984)
D.M. Hunten, T.M. Donahue, Annu. Rev. Earth Planet. Sci. **4**, 265–292 (1976)
D.M. Hunten, R.O. Pepin, J.C.G. Walker, Icarus **69**, 532–549 (1987)
G. Igarashi, in *Volatiles in the Earth and Solar System*, ed. by K. Farley, AIP Conf. Proc. vol. 341. 1995, pp.70–80
M. Ikoma, H. Genda, Astrophys. J. **648**, 696–706 (2006)
M. Ikoma, H. Genda, Astrophys. J. **649** (2006, in press)
M. Ishiwatari, S.-I. Takehiro, K. Nakajima, Y.-Y. Hayashi, J. Atmos. Sci. **59**, 3223–3238 (2002)
B.M. Jahn, F.Y. Wu, C.H. Lo, C.H. Tsai, Chem. Geol. **157**, 119–146 (1999)
S.B. Jakobsen, Annu. Rev. Earth Planet. Sci. **33**, 531–570 (2005)
B.M. Jakosky, T.J. Ahrens, *Proc. Lun. Planet. Sci. Conf. 10* (Pergamon, New York, 1979), pp. 2729–2739
B.S. Kamber, K.D. Collerson, J. Geophys. Res. **104**, 25479–25491 (1999)
B.S. Kamber, M.T. Whitehouse, R. Bolhar, S. Moorbath, Earth Planet. Sci. Lett. **240**, 276–290 (2005)
J.F. Kasting, Icarus **74**, 472–494 (1988)
J.F. Kasting, Orig. Life Evol. Biosphere **20**, 199–231 (1989)
Kelvin, Nature **51**, 438–440 (1895)
L. Keszthelyi, A.S. McEwen, G.J. Taylor, Icarus **141**, 415–419 (1999)
J.L. Kirschvink, in *The Proterozoic Biosphere*, ed. by J.W. Schopf, C. Klein (Cambridge University Press, Cambridge, 1992), pp. 51–52.
T. Kleine, K. Mezger, C. Münker, H. Palme, Nature **418**, 952–955 (2002)
T. Kleine, K. Mezger, C. Munker, H. Palme, A. Bischoff, Geochim. Cosmochim. Acta **68**, 2935–2946 (2004)
T. Kleine, K. Mezger, H. Palme, E. Scherer, C. Münker, Geochim. Cosmochim. Acta **69**, 5805–5818 (2005a)
T. Kleine, H. Palme, K. Mezger, A.N. Halliday, Science **310**, 1671–1674 (2005b)
L.P. Knauth, D.R. Lowe, GSA Bull. **115**, 566–580 (2003)
A.H. Knoll, *Life on a Young Planet: The First Three Billion Years of Evolution on Earth* (Princeton Univ. Press, Princeton, 2003)
E. Kokubo, S. Ida, J. Makino, Icarus **148**, 419–436 (2000)
S.J. Kortenkamp, E. Kokubo, S.J. Weidenschilling, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (The Univ. of Arizona Press, Tucson, 2000), pp. 85–100
A.F. Koster van Groos, J. Geophys. Res. **93**, 8952–8958 (1988)
J.D. Kramers, I.N. Tolstikhin, Chem. Geol. **139**, 75–110 (1997)
Y.N. Kulikov, H. Lammer, I. Herbert, M. Lichtenegger, T. Penz, D. Breuer, T. Spohn, R. Lundin, H.K. Biernat (2007), this issue, doi:10.1007/s11214-007-9192-4
S.-T. Kwon, G.R. Tilton, M.H. Grnnenfelder, in *Carbonatites—Genesis and Evolution*, ed. by K. Bell (Unwin-Hyman, London, 1989), pp. 360–387
F.T. Kyte, A. Shukolyukov, G.W. Lugmair, D.R. Lowe, G. Byerly, Geology **31**, 283–286 (2003)
J.A. Lake, Nature **331**, 184–186 (1988)
M.A. Lange, T.J. Ahrens, Icarus **51**, 96–120 (1982)
D.-C. Lee, A.N. Halliday, Nature **388**, 854–857 (1997)
D.-C. Lee, A.N. Halliday, G.A. Snyder, L.A. Taylor, Science **278**, 1098–1103 (1997)
D.-C. Lee, A.N. Halliday, I. Leya, R. Wieler, U. Wiechert, Earth Planet. Sci. Lett. **198**, 267–274 (2002)
H.F. Levison, M. Duncan, Icarus **127**, 3–16 (1997)
H.F. Levison, L. Dones, C.R. Chapman, S.A. Stern, M.J. Duncan, K.J. Zahnle, Icarus **151**, 286–306 (2001)
J.S. Lewis, R.G. Prinn, *Planets and Their Atmospheres—Origin and Evolution* (Academic, Orlando, 1984)
C. Liebske, B. Schmickler, H. Terasaki, B.T. Poe, A. Suzuki, R. Ando, K. Funakoshi, D.C. Rubie, Earth Planet. Sci. Lett. **240**, 589–604 (2005)
T.C. Liew, C.C. Milisenda, A.W. Hofmann, Geol. Rundsch. **80**, 279–288 (1991)
J.J. Lissauer, Annu. Rev. Astron. Astrophys. **31**, 129–174 (1993)
K. Lodders, B. Fegley, *The Planetary Scientist's Companion* (Oxford Univ. Press, Oxford, 1998)
D.R. Lowe, G.R. Byerly, Geology **11**, 668–671 (1986)

D.R. Lowe, G.R. Byerly, F. Asaro, F. Kyte, Science **245**, 959–962 (1989)
P. Lowell, *Mars* (Houghton, Mifflin and Co., Boston, 1895)
P. Lowell, *Mars and Its Canals* (MacMillan, New York, 1906)
P. Lowell, *The Evolution of Worlds* (MacMillan, New York, 1909)
J.I. Lunine, A. Morbidelli, J. Chambers, L.A. Leshin, Icarus **165**, 1–8 (2003)
K.A. Maher, D.J. Stevenson, Nature **331**, 612–614 (1988)
A. Markowski, G. Quitté, A.N. Halliday, T. Kleine, Earth Planet. Sci. Lett. **242**, 1–15 (2006)
T. Matsui, Y. Abe, Nature **319**, 303–305 (1986)
C.P. McKay, Geophys. Res. Lett. **27**, 2153–2156 (2000)
C.P. McKay, in *The Extreme Proterozoic: Geology, Geochemistry, and Climate*, ed. by G.S. Jenkins, M.A.S. McMenamin, C.P. McKay, L. Sohl. Geophysical Monograph, vol. 146 (American Geophysical Union, Washington, 2004), pp. 193–198
A.S. McEwen et al., Science **281**, 87–90 (1998)
H.J. Melosh, *Impact Cratering: A Geological Process* (Oxford University Press, New York, 1989)
C. Mileikowsky, F.A. Cucinotta, J.W. Wilson, B. Gladman, G. Horneck, L. Lindgren, J. Melosh, H. Rickman, M. Valtonen, J.Q. Zheng, Planet. Space Sci. **48**, 1107–1115 (2000)
S.L. Miller, Science **117**, 528–529 (1953)
H. Mizuno, K. Nakazawa, C. Hayashi, Earth Planet. Sci. Lett. **50**, 202–210 (1980)
H. Mizuno, G.W. Wetherill, Icarus **59**, 74–86 (1984)
S.J. Mojzsis, T.M. Harrison, R.T. Pidgeon, Nature **409**, 178–181 (2001)
A. Morbidelli, J. Chambers, J.I. Lunine, J.-M. Petit, G.B. Valsecchi, F. Robert, K.E. Cyr, Meteor. Planet. Sci. **35**, 1309–1320 (2000)
A. Morbidelli, J.-M. Petit, B. Gladman, J.E. Chambers, Meteor. Planet. Sci. **36**, 371–380
D.T. Murphy, B.S. Kamber, K.D. Collerson, J. Petrol. **44**, 39–53 (2003)
S. Nakajima, Y.-Y. Hayashi, Y. Abe, J. Atmospheric Sci. **49**, 2256–2266 (1992)
G. Neukum, B.A. Ivanov, in *Hazards due to Comets and Asteroids*, ed. by T. Gehrels (University of Arizona Press, Tucson, 1994), pp. 359–416
G. Neukum, B.A. Ivanov, W.K. Hartmann, in *Chronology and Evolution of Mars*, ed. by R. Kallenbach, J. Gleiss (Kluwer, Dordrecht, 2001), pp. 55–86, reprinted from Space Sci. Rev. **96**(1–4)
E.G. Nisbet, Precambr. Res. **19**, 111–118 (1982)
E.G. Nisbet, Geol. Mag. **122**, 84–94 (1985)
E.G. Nisbet, Episodes **14**, 327–331 (1991)
E.G. Nisbet, Nature **380**, 291 (1996)
E.G. Nisbet et al., Space Sci. Rev. (2007), this issue, doi:10.1007/s11214-007-9175-5
T. Owen, P. Mahaffy, H.B. Niemann, S. Atreya, T. Donahue, A. Bar-Nun, I. de Pater, Nature **402**, 269–270 (1999)
M. Ozima, F.A. Podosek, *Noble Gas Geochemistry* (Cambridge University Press, Cambridge, 2002)
N. Pace, G.J. Olsen, C.R. Woese, Cell **45**, 325–326 (1986)
C.C. Patterson, Geochim. Cosmochim. Acta **10**, 230–237 (1956)
R.O. Pepin, Icarus **92**, 2–79 (1991)
R.T. Pierrehumbert, Nature **429**, 646–649 (2004)
D. Pollard, J.F. Kasting, J. Geophys. Res. **110**, C07010 (2005). doi:10.1029/2004JC002525
D. Porcelli, R.O. Pepin, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (The Univ. of Arizona Press, Tucson, 2000), pp. 435–458
S.N. Raymond, T.R. Quinn, J.I. Lunine, Icarus **168**, 1–17 (2004)
A.E. Ringwood, Geochim. Cosmochim. Acta **21**, 295–296 (1961)
W.W. Rubey, Bull. Geol. Soc. Am. **62**, 1111–1147 (1951)
T. Rushmer, W.G. Minarik, G.J. Taylor, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (The Univ. of Arizona Press, Tucson, 2000), pp. 227–243
M.J. Russell, N.T. Arndt, Biogeosciences **2**, 97–111 (2005)
S.S. Russell, G. Srinivasan, G.R. Huss, G.J. Wasserburg, G.J. MacPherson, Science **273**, 757–762 (1996)
G. Ryder, C. Koeberl, S. Mojzsis, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (The Univ. of Arizona Press, Tucson, 2000), pp. 475–492
G. Ryder, J. Geophys. Res. **107**, 10 (2002). doi:1029/2001JE001583
G. Ryder, Astrobiology **3**, 3–6 (2003)
I.-J. Sackmann, A.I. Boothroyd, Astrophys. J. **583**, 1024–1039 (2003)
I.-J. Sackmann, A.I. Boothroyd, K.E. Kraemer, Astrophys. J. **418**, 457–468 (1993)
V.S. Safronov, Evolution of the protoplanetary cloud and formation of the Earth and the Planets. NASA TT F-677, 1972
C. Sagan, G. Mullen, Science **177**, 52–56 (1972)

S. Sasaki, in *Origin of the Earth*, ed. by H.E. Newsom, J.H. Jones (Oxford University Press, Oxford, 1990), pp. 195–209
S. Sasaki, K. Nakazawa, Earth Planet. Sci. Lett. **89**, 323–334 (1988)
A. Scherstén, T. Elliott, C. Hawkesworth, S.S. Russell, O. Masarik, Earth Planet. Sci. Lett. **241**, 530–542 (2006)
M. Schidlowski, Nature **333**, 313–318 (1988)
G. Schubert, D. Turcotte, P. Olson, *Mantle Convection in the Earth and Planets* (Cambridge University Press, 2001)
D. Schwartzman, *Life, Temperature, and the Earth* (Columbia University Press, 2002), 272 pp.
M. Sekiya, K. Nakazawa, C. Hayashi, Earth Planet. Sci. Lett. **50**, 197–201 (1980a)
M. Sekiya, K. Nakazawa, C. Hayashi, Prog. Theor. Phys. **64**, 1968–1985 (1980b)
M. Sekiya, C. Hayashi, K. Kanazawa, Prog. Theor. Phys. **66**, 1301–1316 (1981)
E.L. Shock, J.P. Amend, M.Y. Zolotov, in *Origin of Earth and Moon*, ed. by R.M. Canup, K. Righter (University of Arizona Press, Tucson, 2000), pp. 527–543
J.M. Sinton, R.S. Detrick, J. Geophys. Res. **97**, 197–216 (1992)
N.H. Sleep, J. Geophys. Res. **105**(17), 563–17578 (2000)
N.H. Sleep, in *Treatise on Geophysics, vol. 9. Evolution of the Earth*, ed. by D.J. Stevenson (Elsevier, 2007)
N.H. Sleep, A.M. Hessler, Earth Planet. Sci. Lett. **241**, 594–602 (2006)
N.H. Sleep, R.T. Langan, Adv. Geophys. **23**, 1–23 (1981)
N.H. Sleep, K. Zahnle, J. Geophys. Res. **103**, 28529–28544 (1998)
N.H. Sleep, K. Zahnle, J. Geophys. Res. **106**, 1373–1400 (2001)
N.H. Sleep, K.J. Zahnle, J.F. Kasting, H.J. Morowitz, Nature **342**, 139–142 (1989)
N.H. Sleep, K.J. Zahnle, P.S. Neuhoff, Proc. Nat. Acad. Sci. **98**, 3666–3672 (2001)
V.S. Solomatov, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (University of Arizona Press, Tucson, 2000), pp. 413–433
J.R. Spencer, J.A. Rathbun, L.D. Travis, L.K. Tamppari, L. Barnard, T.Z. Martin, A.S. McEwen, Science **288**, 1198–1201 (2000)
F.J. Stadermann, E. Heusser, E.K. Jessberger, S. Lingner, D. Stöffler, Geochim. Cosmochim. Acta **55**, 2339–2349 (1991)
D.J. Stevenson, in *Earth's Earliest Biosphere*, ed. by J.W. Schopf (Princeton University Press, Princeton, 1983), pp. 32–40
D.J. Stevenson, Annu. Rev. Earth Planet. Sci. **15**, 271–315 (1987)
D.J. Stevenson, in *Origin of the Earth*, ed. by H.E. Newsom, J.H. Jones (Oxford University Press, London, 1990), pp. 231–249
D.J. Stevenson, Earth Planet. Sci. Lett. **208**, 1–11 (2003)
S.R. Taylor, *Solar System Evolution* (Cambridge University Press, Cambridge, 1993)
F. Tera, D.A. Papanastassiou, G.J. Wasserburg, Earth Planet. Sci. Lett. **22**, 1–21 (1974)
E.W. Thommes, M.J. Duncan, H.F. Levison, Astron. J. **123**, 2862–2883 (2002)
J. Touma, in *Origin of Earth and Moon*, ed. by R.M. Canup, K. Righter (University of Arizona Press, Tucson, 2000), pp. 165–178
J. Touma, J. Wisdom, Astron. J. **108**, 1943–1961 (1994)
J. Touma, J. Wisdom, Astron. J. **115**, 1653–1663 (1998)
H.C. Urey, Geochim. Cosmochim. Acta **1**, 209–277 (1951)
J.W. Valley, W.H. Peck, E.M. King, S.A. Wilde, Geology **30**, 351–354 (2002)
J.W. Valley, J.S. Lackey, A.J. Cavosie, C.C. Clechenko, M.J. Spicuzza, M.A.S. Basei, I.N. Bindeman, V.P. Ferreira, A.N. Sial, E.M. King, W.H. Peck, A.K. Sinha, C.S. Wei, Contributions Mineral. Petrol. **150**, 561–580 (2005)
P. van Thienen et al., Space Sci. Rev. (2007), this issue, doi:10.1007/s11214-007-9149-7
R. von Huene, D.W. Scholl, Rev. Geophys. **29**, 279–316 (1991)
W.R. Ward, in *Origin of the Earth and Moon*, ed. by R.M. Canup, K. Righter (The Univ. of Arizona Press, Tucson, 2000), pp. 65–289
P.H. Warren, E.A. Jerde, G.W. Kallemeyn, Earth Planet. Sci. Lett. **91**, 245–260 (1989)
S.G. Warren, R.E. Brandt, T.C. Grenfell, C.P. McKay, J. Geophys. Res. **107**(C10), 3167 (2002). doi:10.1029/2001JC001123
A.J. Watson, T.M. Donahue, J.C.G. Walker, Icarus **48**, 150–166 (1981)
S.J. Weidenschilling, J.N. Cuzzi, in *Protostars and Planets III*, ed. by E.H. Levy, J.I. Lunine (Univ. of Arizona Press, Tucson, 1993), pp. 1031–1060
B.P. Weiss, J.L. Kirshvink, F.J. Baudenbacher, H. Vali, N.T. Peters, F.A. Macdonald, J.P. Wikswo, Science **290**, 791–795 (2000)
L.E. Wells, J.C. Armstrong, G. Gonzalez, Icarus **162**, 38–46 (2003)
G.W. Wetherill, Proc. Lunar Sci. Conf. **6**, 1539–1561 (1975)

G.W. Wetherill, Science **228**, 877–879 (1985)
G.W. Wetherill, in *Origin of the Moon*, ed. by W.K. Hartmann et al. (Lunar Planetary Institute, Houston, 1986), pp. 519–550
W.B. Whitman, D.C. Coleman, W.J. Wiebe, Proc. Natl. Acad. Sci. **95**, 6578–6583 (1998)
S.A. Wilde, J.W. Valley, W.H. Peck, C.M. Graham, Nature **409**, 175–178 (2001)
D.E. Wilhelms, The Geologic History of the Moon, U.S.G.S. Professional Paper 1348, 1987
D.S. Woolum, P. Cassen, Meteor. Planet. Sci. **34**, 897–907 (1999)
B.E. Wood, H.-R. Muller, G.P. Zank, J.L. Linsky, Astrophys. J. **574**, 412–425 (2002)
B.E. Wood, H.-R. Muller, J.L. Linsky, G.P. Zank, S. Redfield, Astrophys. J. **628**, L143–L146 (2005)
B.J. Wood, A.N. Halliday, Nature **437**, 1345–1348 (2005)
Q.Z. Yin, S.B. Jacobsen, K. Yamashita, J. Blichert-Toft, P. Télouk, F. Albarède, Nature **418**, 949–952 (2002)
T. Yoshino, M.J. Walter, T. Katsura, Nature **422**, 154–157 (2003)
K.J. Zahnle, in *Origins*, ed. by C.E. Woodward, J.M. Shull, H.A. Thronson. ASP Conference Series, vol. 148, 1998, pp. 364–391
K. Zahnle, J. Kasting, Icarus **68**, 462–480 (1986)
K.J. Zahnle, J.F. Kasting, J.B. Pollack, Icarus **74**, 62–97 (1988)
K.J. Zahnle, N.H. Sleep, in *The Early Earth: Physical Chemical and Biological Development*, ed. by C.M. Fowler, C.J. Ebinger, C.J. Hawkesworth. Geol. Soc. London Spec. Pub., 199, 2002, pp. 231–257
K.J. Zahnle, N.H. Sleep, in *Comets and the Origin and Evolution of Life*, ed. by P. Thomas, C.F. Chyba, C.P. McKay (Springer, 1997), pp. 175–208
K. Zahnle, N.H. Sleep, in *Comets and the Origin and Evolution of Life*, 2nd edn, ed. by P.J. Thomas, R.D. Hicks, C.F. Chyba, C.P. McKay (Springer, Berlin, 2006), pp. 207–251
R.E. Zartman, S.M. Haines, Geochim. Cosmochim, Acta **52**, 1327–1339 (1988)