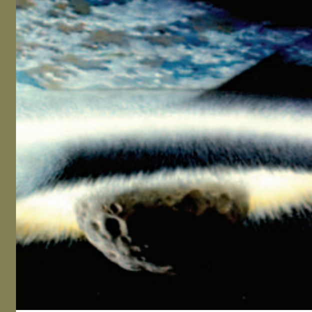

Image courtesy of NASA Ames Research Center (Artist: Don Davis)

Earth's Earliest Atmosphere

Kevin J. Zahnle[1]

The aftermath of the Moon-forming impact left Earth with a hot, CO_2-rich steam atmosphere. Water oceans condensed from the steam after 2 Myr, but for some 10–100 Myr the surface stayed warm (~500K), the length of time depending on how quickly the CO_2 was removed into the mantle. Thereafter a lifeless Earth, heated only by the dim light of the young Sun, would have evolved into a bitterly cold ice world. The cooling trend was frequently interrupted by volcanic- or impact-induced thaws.

Keywords: Hadean Earth, Moon-forming impact, origin, evolution of the atmosphere, zircon

INTRODUCTION

The newly made Earth is widely and enduringly pictured as a world of exuberant volcanoes, exploding meteors, huge craters, stifling heat, and billowing sulfurous steams—a world of fire and brimstone punctuated with blows to the head. The popular image has drawn to it the name Hadean, a name that celebrates our mythic roots. But the infernal image of the earliest Earth also has purely scientific roots. A hot early Earth is a consequence of fast planetary growth. Any lingering doubts were vaporized by the success of the Moon-forming impact hypothesis (Canup 2004). Earth as we know it emerged from a fog of silicate vapor.

THE YOUNG SUN

The Sun took ~50 million years to contract to the Main Sequence (Fig. 1). Contraction stopped when the Sun's core became hot and dense enough to fuse hydrogen into helium. The stable state in which starlight is fueled by hydrogen burning in the center of a star is called the Main Sequence. It lasts as long as the hydrogen fuel in the core lasts. While on the Main Sequence, the Sun steadily brightens as its mean molecular weight increases. The standard model predicts that the Sun was only 71% as bright as it is now when it reached the Main Sequence and that it brightened 7% over the next billion years.

The faint young Sun imposed a stringent constraint on the climate of the young Earth (Sagan and Mullen 1972). Without potent greenhouse gases, the early Earth should have been at most times and places frozen over.

The only plausible way to make the young Sun brighter is to make it more massive. Adding 6% more mass would make it as bright as it is now (Sackmann and Boothroyd 2003). The Sun does lose mass through the solar wind, but at current rates it would lose only 0.01% of its mass over 4.5 Gyr. By studying stellar winds from nearby stars that are Sun-like but younger, Wood et al. (2002) deduced that our Sun has lost less than 0.5% of its mass since it reached the Main Sequence. This is too small to be important. Evidence bounding mass loss from still younger stars is indirect, but the empirical upper limit on X-ray emission implies a parallel upper limit on mass loss that is less than 1% of the initial mass. The range of solar evolutions permitted by mass loss is shown in Figure 1.

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 (Fig. 1). 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) is related to the strength of the magnetic field, which in turn is gener-

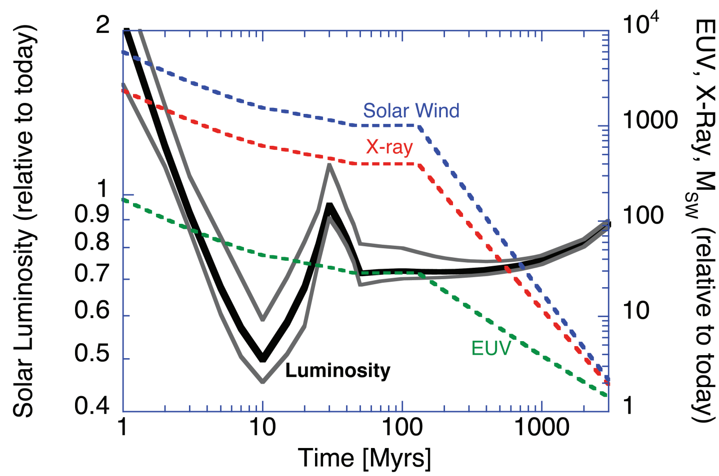

Figure 1 The first 3 billion years of solar evolution. The solid curves show luminosity evolution. The Sun reached the Main Sequence after 50 Myr. Main Sequence luminosity evolution follows Sackmann and Boothroyd (2003). Pre–Main Sequence evolution is adapted from D'Antona and Mazzitelli (1994). Inconstant luminosity before reaching the Main Sequence is a consequence of gravitational settling. The range of uncertainty (shown by grey solid curves) is determined by mass loss. Mass loss follows Wood et al. (2002). Sensitivity to mass loss is scaled from Sackmann and Boothroyd (2003). Dashed curves show nominal solar wind (Msw), X-ray, and extreme ultraviolet (EUV) histories (Wood et al. 2002). The observed scatter in X-ray luminosities of stars like the young Sun implies an order of magnitude uncertainty in these quantities for the Sun during the Hadean.

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ated 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.

ORIGIN OF EARTH'S ATMOSPHERE

Earth's atmosphere is often described as secondary, a word that implies a history. The primary atmosphere is defined as gas captured gravitationally from the solar nebula (the primordial cloud of gas and dust from which the Sun and planets were formed). Like the Sun itself, a primary atmosphere is overwhelmingly made of hydrogen. In principle small planets like Earth could have captured significant primary atmospheres, depending on how long the nebula lasted (Hayashi et al. 1979).

Traditional arguments for and against a primary atmosphere are based on the abundances of noble gases (FIG. 2). A primary atmosphere provides a way to inject ^{3}He and solar neon into a molten mantle. But atmospheric neon argues otherwise. First, the $^{20}Ne/^{36}Ar$ ratio is ~30 in the Sun but ~0.3 in the atmospheres of Earth, Mars, and Venus—a hundred-fold discrepancy. It is even more telling to compare neon to nitrogen. Nitrogen is one of the most volatile elements apart from the noble gases. The solar N/Ne ratio is unity. In Earth's atmosphere that ratio is 86,000. Either Ne escaped from Earth 86,000 times more efficiently than N, or the major source of N was in a condensate of some kind. If N was delivered in a condensate it is by definition secondary.

Traditionally, the secondary atmosphere is composed of volatiles delivered to Earth in solid bodies (akin to meteorites) that degassed after a primary atmosphere, if any, was lost. This is sometimes taken to mean that Earth's atmosphere degassed from the solid Earth into a primordial vacuum. However, most volatiles accreted by Earth as solids would have entered the atmosphere directly on impact (Ahrens et al. 1989). This would generally be the case for asteroids and meteors once collision velocities became high enough (collision velocities get bigger as the planet gets bigger), and it would probably be the case for comets at pretty much any collision velocity.

Another factor affecting atmospheric composition is that gases escape to space. The active young Sun was a powerful source of ultraviolet radiation (FIG. 1). Far UV wavelengths between 100 and 200 nm are absorbed by H_2O and CO_2 and cause these molecules to break up into atoms or into simpler molecules such as H_2 and CO. The survivors are in general poor infrared coolants. The more energetic UV (EUV, <100 nm) is strongly absorbed at very high altitudes where only poor infrared coolants remain. Without effective

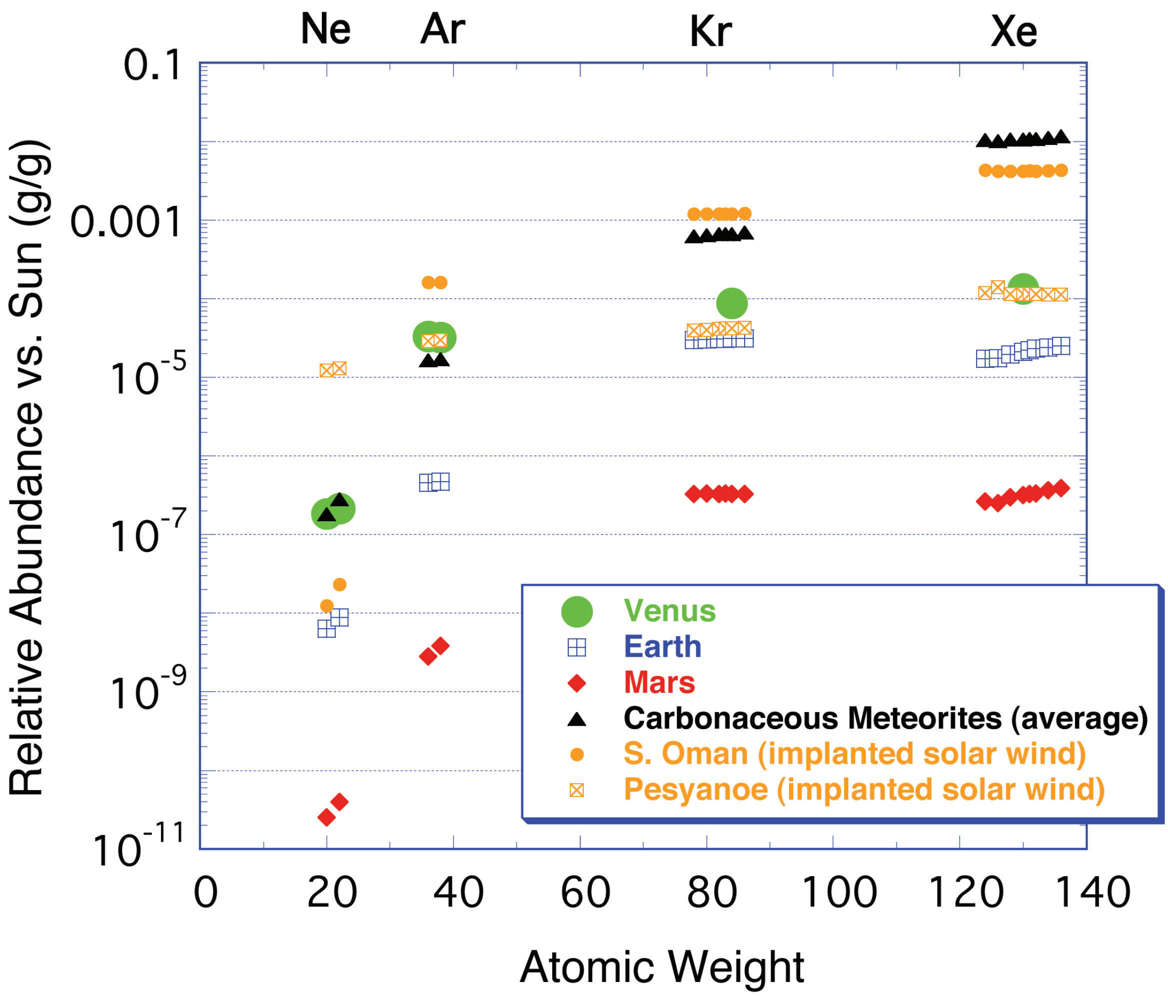

FIGURE 2 Noble gas isotopic abundances are shown relative to their abundances in the Sun. A purely solar abundance pattern would be a horizontal line. Apart from Xe, the noble gases on Earth and Mars resemble those in carbonaceous meteorites (Pepin 1991), although the planets are greatly depleted. Xenon is discrepant both in quantity and isotopic pattern. Evidence that Earth experienced vigorous hydrogen escape is preserved in the mass-fractionated isotopes of Ne and Xe (Ozima and Podosek 2002). Xenon—the heaviest gas in the atmosphere—is strongly mass fractionated compared to any plausible source; hydrogen escape to space can produce the observed isotopic fractionation (Pepin 1991). The required hydrogen flux to space is high but within the range permitted by EUV emission from the active young Sun. Venus more closely resembles the solar wind noble gases implanted 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).

coolants the EUV makes the thin gas very hot. If hydrogen is abundant the hot gas can balance its energy budget by hydrogen escape. Evidence that Earth experienced vigorous hydrogen escape is preserved in the mass-fractionated isotopes of Ne and Xe (FIG. 2). Missing radiogenic xenon provides another strong argument that xenon escaped (Porcelli and Pepin 2000).

Water catches more interest than any other volatile, perhaps because water is more interesting than noble gases and its behavior is simpler than carbon's. Most water accreted by Earth was probably delivered in the form of hydrous silicates. Water can also be made in situ by oxidizing H_2 or by oxidizing organic molecules (Abe et al. 2000), but neither works well for Earth: the former gives a D/H ratio that is too low while the latter gives a C/H ratio that is too high. The hydrous silicates were themselves secondary, products of chemical reactions with liquid water. The water was first condensed as ice, either 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), or in comets. The likelihood that any known source could deliver an ocean of water to Earth after the Moon-forming impact is demonstrably small (Levison et al. 2001).

AFTER THE MOON-FORMING IMPACT

Although the Moon-forming impact may not have been the last big impact, it probably was the last time that Earth was hit by another planet. The impact is currently thought to have occurred at around 40–50 Ma (see Halliday 2006). By coincidence the Sun reached the Main Sequence at ~50 Ma. This is a good place to take up Earth's story (FIG. 3).

Most of the mantle was melted by the Moon-forming impact, and some of it was vaporized (Canup 2004). Immediately after the impact, the atmosphere was mostly rock vapor topped by ~2500K silicate clouds. For a thousand years the silicate clouds defined the visible face of the planet. The new 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 fell out, were the volatiles. Because convective cooling requires that every parcel be brought to the cloud tops to cool, the mantle should have largely degassed, with the notable exception of water, which remained mostly in the molten mantle and which degassed as the mantle froze. When the silicates were gone, a hot CO_2–CO–H_2O–H_2 atmosphere remained, although at first most of Earth's water would have been dissolved in the molten mantle. Also left in the atmosphere were nitrogen, the noble gases, and possibly moderately volatile elements such as Zn and Pb, some of which did not fully condense until after the surface of the magma ocean froze.

How thick the atmosphere was is debatable. The Moon-forming impact may or may not have expelled a significant fraction of Earth's pre-existing volatiles, and Earth may or may not have had abundant volatiles to lose. A primary H_2 atmosphere, because of its low mean molecular weight,

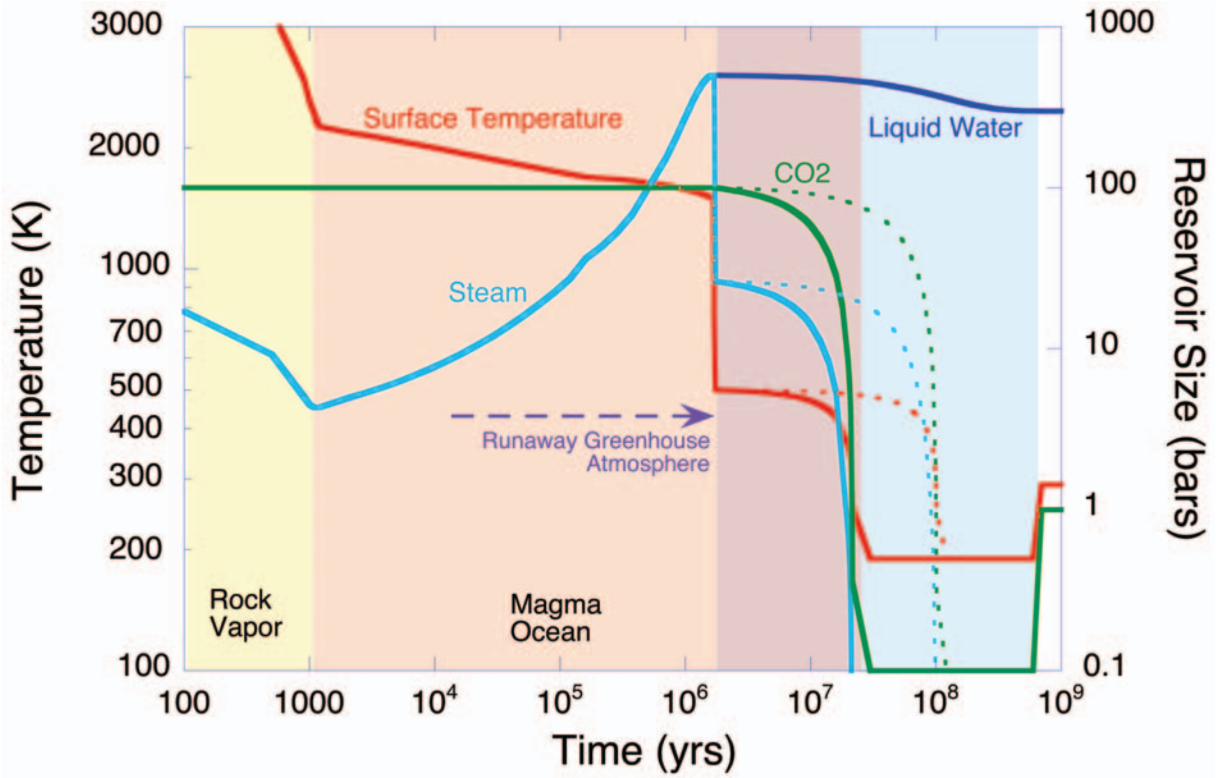

FIGURE 3 A history of temperature, water, and CO_2 during the Hadean. The curves show the surface temperature and the amount of water and CO_2 in the atmosphere and hydrosphere after the Moon-forming impact. Earth's water oceans today are equivalent to 270 bars of steam. Earth was initially enveloped in rock vapor for 1000 years. The magma ocean lasted some 2 Myr, prolonged by the runaway greenhouse effect (FIG. 4). Most of Earth's water degassed as the mantle solidified. After the mantle froze, geothermal heat could no longer sustain a steam atmosphere, and the steam atmosphere condensed to form a warm (~500K) water ocean under ~100 bars of CO_2. This warm wet early Earth would have lasted as long as Earth's CO_2 stayed in the atmosphere. For specificity, I have assumed that CO_2 is subducted into the mantle on either a 20 Myr (solid curves) or 100 Myr (dashed curves) timescale. The asymptotic level of CO_2 is presumed to be controlled by chemical weathering of oceanic crust and abundant impact ejecta. Prior to the origin of life, in the absence of an abundant potent greenhouse gas, the surface should have been icy, although occasional impacts would have caused thaws. After the Late Heavy Bombardment, the CO_2 is allowed to return to ~1 bar in order that the surface be clement; this is arbitrary.

would have readily escaped. But a secondary atmosphere would have to be pushed off. 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. Recent theory suggests that the answer depends on whether there had been a deep liquid-water ocean on the surface. A thin atmosphere above a thick water ocean can be expelled. Otherwise the atmosphere is retained (Genda and Abe 2005). One notes that water is retained in either event. The view taken here is that the planet that became Earth was water rich.

Thermal blanketing by the atmosphere controlled the cooling rate of the magma ocean (Fig. 3). When hotter than 2000K, cooling rates were high, although well short of what they would be for a bare planet (Abe et al. 2000). But after the surface cooled below ~1700K, the thermal blanketing became extremely effective and the atmosphere relaxed into a runaway greenhouse state (Fig. 4) sustained by sunlight and geothermal heat flow. The runaway greenhouse limit for Earth is ~310 W/m^2. With sunlight accounted for, the runaway greenhouse limit tells us that the geothermal heat flow was ~140 W/m^2 (Fig. 4). As the Earth cooled the surface was kept molten by a stabilizing feedback between water vapor's control over the surface temperature and water's solubility in the melt (Abe and Matsui 1988). Because of this feedback, the mantle degassed most of its water towards the end of the runaway greenhouse phase (Zahnle et al. 1988). Once the runaway greenhouse was in place, it took ~2 million years to cool the mantle to the freezing point. This history is depicted in Fig. 3.

Once the mantle was mostly frozen, the mantle cooled by solid-state convection with a vigor set by the viscosity at the top of the mantle. Heat flow was too small to affect the climate. The mid-ocean ridges, which are somewhat analogous, suggest that the heat flow was no more than 1–10 W/m^2. At this point the runaway greenhouse collapsed and the steam rained out (at a modest rate of about 1 m/yr). Thereafter the surface was solid and cool and mostly under the waves.

After the Deluge

How hot it was at Earth's surface depends on how much CO_2 was present in the atmosphere and for how long. For as long as most of Earth's CO_2 remained in the atmosphere, the surface temperature would have been ~500K (Fig. 4). Presumably carbonate rock formed quickly during hydrothermal circulation through fresh crust, but the capacity of the crust to store carbonate is limited. At any one time, available divalent cations in the uppermost crust could fix the molar equivalent of ~10 bars of CO_2. The oceanic crust recycles on a 1 Myr timescale, resulting in a global heat flow on the order of 1 W/m^2. Provided that carbonates could subduct into the mantle, it could have taken as little as 10 Myr to remove 100 bars of CO_2. Today most subducted carbonate enters the mantle rather than erupting through arc volcanoes. A hotter mantle made carbonates less stable, but the hotter mantle was also less viscous, letting foundering blocks sink more quickly. If the carbonates did not reach the mantle, the bulk of the CO_2 would have

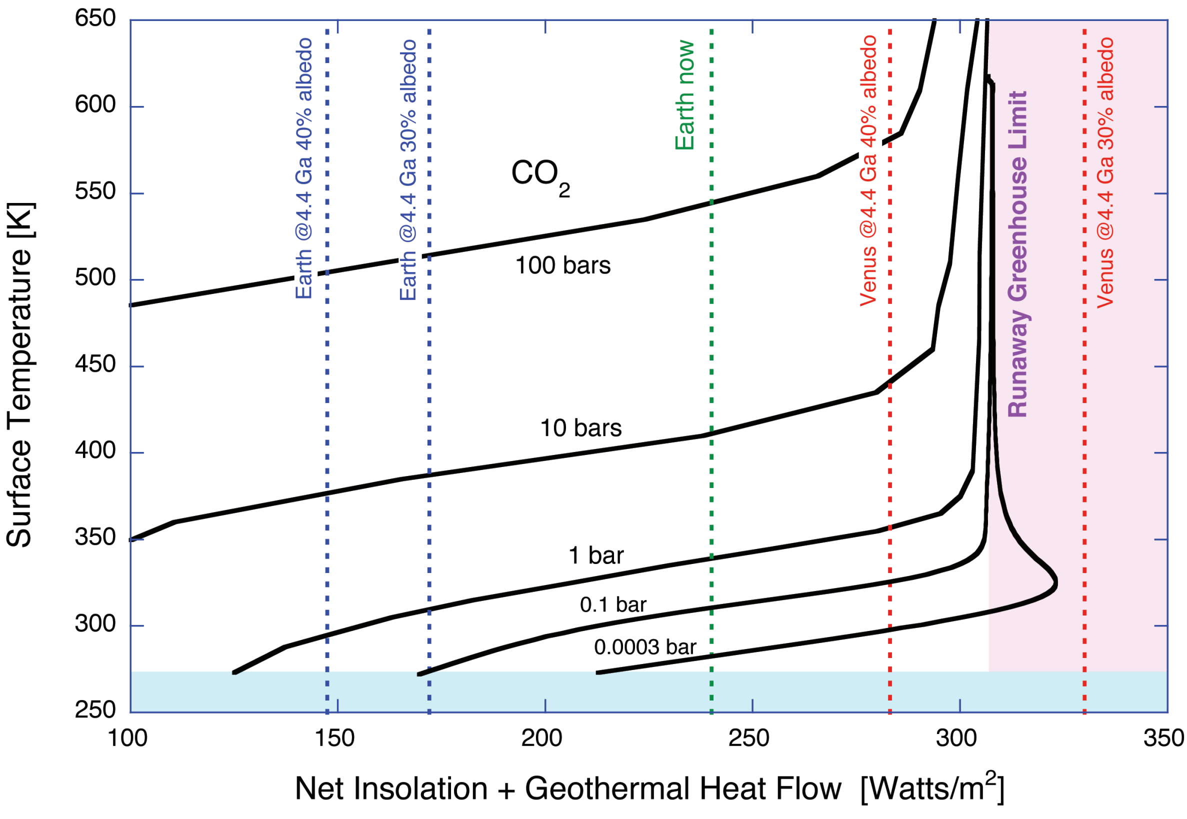

Figure 4 The H_2O–CO_2 greenhouse effect. This plot shows the surface temperature as a function of radiated heat for different amounts of atmospheric CO_2 (after Abe 1993). The radiated heat is the sum of absorbed sunlight (net insolation) and geothermal heat flow. Net insolation takes into account reflection. Net insolations for Earth and Venus at ca. 4.4 Ga (after the Sun reached the Main Sequence) are shown at 30% and 40% albedo. The albedo used here refers to all wavelengths of sunlight, visible and invisible. The higher albedo may be appropriate for a cloudy atmosphere. The plot shows that the atmosphere "runs away" if radiated heat exceeds 310 W/m^2. In a runaway, the surface temperature rises to the next buffer, which for Earth would be the melting point of rocks. Note that CO_2 does not by itself cause a runaway. Earth entered the runaway greenhouse state only ephemerally after big impacts that generated big pulses of geothermal heat. Venus, on the other hand, would have fallen into the runaway state when its albedo dropped below 35%.

remained in the atmosphere and the surface would have remained at ~500K unless there were stable continental platforms on which to put carbonate rocks (Sleep et al. 2001).

By contrast, hydrous minerals are not very stable at high temperatures and modest pressures. If they survived a fast passage to the mantle, they may not have stayed there. They ought instead to have formed water-rich melts at the base of the magma ocean, which would have ascended as proto-granitic plumes. We therefore expect that the early Hadean mantle was dry and that the early water oceans were if anything deeper than they later became.

The argument that the early oceans were deep presumes that as long as the mantle was vigorously convective, every parcel visited the surface to cool, and therefore its water content was set by conditions near the surface, where hydrous minerals were unstable. Implicit is the assumption that the mantle convected as a whole. If instead the mantle convected in layers, the greater stability of hydrous phases at high pressure becomes relevant. This opens the possibility that substantial amounts of water, initially incorporated as solute in magma, could have remained in the lower mantle. Later, when layered convection broke down, the deep water degassed. In this way it is possible for the oceanic volume to grow over time.

AS COLD AS HADES…

The faint young Sun suggests that, when the Hadean was not infernally hot, it could have been bitterly cold. A temperate Hadean Earth would have needed either enormous geothermal heat flow or abundant potent greenhouse gases. Geothermal heat was insignificant after 4.4 Ga, save immediately following big impacts. Of greenhouse gases the only good candidates are CO_2 and CH_4. (Water vapor is in fact the most important greenhouse gas, but it is a dependent variable, mobilized from oceans and ice sheets as needed.) Methane would be a candidate if there were reducing agents or catalysts to generate it from CO_2 and H_2O. On Earth today methane is mostly of biological origin. Methane is a good candidate for keeping Earth warm once it teemed with life, but it is not clear that there was a big enough source of it when Earth was lifeless.

It takes about one bar of CO_2 to provide enough greenhouse warming to stabilize liquid water at the surface (Fig. 3). Although this represents only about 0.5% of Earth's carbon inventory, it is 3000 times more than is there today. We have suggested that CO_2 would have been scoured from the Hadean atmosphere by chemical reactions of carbonic acid with abundant ultramafic volcanics and impact ejecta (Zahnle and Sleep 2002). The carbonates in the weathered ultramafic sediments—if they subduct—would have left too little CO_2 in the air to avert a snowball Earth.

The resultant ice shell over an early Hadean ocean was, at least in places, thin. For heat flows of 1–10 W/m^2, the ice would be 10 to 100 m thick. Sunlight diffusing through thin ice supplements the geothermal heat and can stabilize the ice thickness at something like 1–2 m (Pollard and Kasting 2005). This ice is thin enough to break easily, allowing gas exchange between the ocean and the atmosphere. In the late Hadean (ca. 4 Ga), when heat flow had on global average dropped to 0.3 W/m^2, we would expect that heat flow was patchy and that over large regions heat flow was still 1–10 W/m^2 and, as a consequence, ice was locally thin.

The late bombardment was another factor affecting the Hadean surface environment (Koeberl 2006). During the Hadean, the average energy flux delivered by impacts was about a tenth that delivered by geothermal heat flow. Given that impact effects are strongly focused on the surface, we might expect impacts to be as important to the surface as geological forces, and occasionally much more important. We have discussed the environmental effects of big impacts in detail elsewhere (Zahnle and Sleep 1997). Here we simply note that a big impact could transform a snowball Earth into a water world and that the change could have lasted for a considerable time, especially if it released pent-up greenhouse gases. For impacts similar to those resulting in the bigger lunar basins, the thaws would have lasted at least 100 years, and there would have been hundreds of such events on Earth. There were probably thousands of impacts big enough to melt the ice. Each such impact triggered a brief impact summer.

ZIRCONS

The chief source of terrestrial data for the Hadean are ancient detrital zircons found in Archean and Proterozoic quartzites (Harrison et al. 2005; Valley et al. 2005). U–Pb dating gives accurate ages as old as 4.4 Ga. Oxygen isotopes provide compelling evidence that rocks on Earth were being chemically altered by liquid water before 4.2 Ga and probably before 4.3 Ga (Valley et al. 2005). The zircons are silent on whether the water temperature was 273K or 500K, but the data strongly suggest that Earth's water was in place by 4.2 Ga. A more controversial argument uses the absence of radiogenic Hf in the zircons to suggest that Lu (the parent)—a more incompatible element than Hf and therefore quicker to segregate into a granitic crust—was already separating from Hf at 4.5 Ga (Harrison et al. 2005). The physical separation of Hf-bearing sediment from Lu-bearing sediment might even imply subaerial weathering. In any case the mere 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. Evidently the processes that built the continents were well underway by 4.4 Ga.

THE ATMOSPHERE ENTERING THE ARCHEAN

Although the Hadean was a time of geologic upheavals and huge climate swings, the system evolved quickly, and Earth's youthful excesses were mostly soon forgotten. It seems reasonable to think that the atmosphere and hydrosphere at the beginning of the Archean were not hugely different from what they are now.

The most important distinctive qualities of the Archean atmosphere are the absence of O_2 and the presence of a strong greenhouse effect. Oxygen's history has been recently reviewed by Canfield (2005). It has been argued that the Archean was very warm (Knauth and Lowe 2003); to our knowledge it has not been argued that the Archean was bitterly cold. If the Archean was warm, potent greenhouse gases were needed to counter the faint Sun (Sagan and Mullen 1972). The leading candidates remain CO_2 and CH_4. Methane is the better choice if the Archean were biologically productive, while CO_2 is the better choice if Earth were lifeless or nearly so.

The early Archean ocean could have been deeper than it is now. There are two reasons to suggest this. One is the expectation that a hotter upper mantle takes up water less easily and degasses water more easily. The other is the inevitable steady loss of hydrogen to space. Hydrogen escape is not negligible (Catling et al. 2001). If methane were the greenhouse gas of the Archean, hundreds of meters of water were lost to space.

A discussion of the early atmosphere seems incomplete without mentioning the most abundant gas in the atmosphere. Earth has 0.78 bars of N_2 in air and a roughly comparable amount in the crust; the mantle inventory appears to be ten times smaller. The crustal reservoir may be linked to biological activity. The small mantle reservoir is isotopically lighter than either of the big reservoirs. This may mean that light nitrogen has been preferentially subducted, or it may mean that the surface inventories have grown heavier by escape of light nitrogen. Overall, these observations imply that before the origin of life there may have been 2 or 3 bars of N_2 in the atmosphere, an amount approaching what we see in the atmosphere of Venus today.

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