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# The Atmospheres of the Terrestrial Planets: Clues to the Origins and Early Evolution of Venus, Earth, and Mars

**Kevin H. Baines**

*University of Wisconsin-Madison*

**Sushil K. Atreya**

*The University of Michigan*

**Mark A. Bullock**

*Southwest Research Institute*

**David H. Grinspoon**

*Denver Museum of Nature and Science*

**Paul Mahaffy**

*NASA Goddard Space Flight Center*

**Christopher T. Russell and Gerald Schubert**

*University of California, Los Angeles*

**Kevin Zahnle**

*NASA Ames Research Center*

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We review the current state of knowledge of the origin and early evolution of the three largest terrestrial planets — Venus, Earth, and Mars — setting the stage for the chapters on comparative climatological processes to follow. We summarize current models of planetary formation, as revealed by studies of solid materials from Earth and meteorites from Mars. For Venus, we emphasize the known differences and similarities in planetary bulk properties and composition with Earth and Mars, focusing on key properties indicative of planetary formation and early evolution, particularly of the atmospheres of all three planets. We review the need for future *in situ* measurements for improving our understanding of the origin and evolution of the atmospheres of our planetary neighbors and Earth, and suggest the accuracies required of such new *in situ* data. Finally, we discuss the role new measurements of Mars and Venus have in understanding the state and evolution of planets found in the habitable zones of other stars.

## I. INTRODUCTION

### 1.1. Venus Spacecraft Data

In the last decade, the exploration of Venus and Mars has experienced a renaissance as space agencies in Europe, Japan, and America have developed and executed a number of missions to Earth's neighbors. Since April 11, 2006, the European Space Agency's (ESA) Venus Express mission has been in orbit, scrutinizing Venus from the ground up. As such, it has accurately determined the thermal structure at hundreds of radio occultation sites from pole-to-pole (e.g.,

Tellman et al., 2008); followed the movements, spatial morphologies, and vertical structures of clouds (e.g., Sánchez-Lavega et al., 2008; Hueso et al., 2012; Markiewicz et al., 2007; Titov et al., 2012; McGouldrick et al., 2008, 2012; Barstow et al., 2012); studied the composition of reactive and dynamically-diagnostic gases in the lower and upper atmosphere and their spatial and temporal variability (e.g., Belyaev et al., 2008; Bézard et al., 2008; Marcq et al., 2008; Irwin et al., 2008; Piccioni et al., 2008; Tsang et al., 2008, 2009; Vandaele et al., 2008; Cottini et al., 2012); and obtained constraints on the composition of its surface and its spatial variability, particularly associated with major

geologic features (e.g., *Mueller et al.*, 2008; *Smrekar et al.*, 2010). Venus Express has also obtained solid evidence for lightning (*Russell et al.*, 2007, 2008) and has sensed and characterized the solar-induced leakage of planetary materials — in particular, H and O — into space (*Barabash et al.*, 2007; *Luhmann et al.*, 2008; *Fedorov et al.*, 2011). As this mission winds down in 2015, current plans are to perform a second attempt to place the Japanese Akatsuki spacecraft [also known as Venus Climate Orbiter (VCO)] in orbit, to continue studies of Venus' circulation and dynamics, particularly the planet's global superrotating wind structure.

## 1.2. Mars Spacecraft Data

The twenty-first century has brought an abundance of both orbiting and surface explorers to Mars, with several additional missions planned for launch by 2020. Starting in early 2004, three heavily instrumented rovers have explored the Red Planet, conducting detailed observations of the planet's geology, surface properties, atmospheric composition, and climate, in particular sampling surface materials and atmospheric trace gases for signs of ancient water and other biologically related materials. Two Mars Exploration Rovers landed on January 3 and 25, 2004, and quickly discovered S-bearing minerals formed within ancient standing bodies of water on the planet's surface (e.g., *Squyres and Knoll*, 2005). On August 6, 2012, the Curiosity rover began exploring the strata of the 5.5-km-tall layered Mount Sharp to elucidate the geologic history of the planet. The Sample Analysis at Mars (SAM) instrument (*Mahaffy et al.*, 2012) onboard Curiosity is of particular interest, as it acquires *in situ* samples of a host of atmospheric gases, including noble gases and their isotopes, light isotopes of C, O, and N, and methane [previously reported by *Mumma et al.* (2009), *Krasnapolsky et al.* (2004), and *Formisano et al.* (2004), but still a matter of much debate], all to assess Mars' history — its origin, evolution, and biological record (*Grotzinger et al.*, 2012). Since their arrival in December 2003, October 2001, and March 2006, respectively, three orbital missions — ESA's Mars Express and NASA's Mars Odyssey and Mars Reconnaissance Orbiter missions — have been continuously surveying the Red Planet for, in particular, evidence of past and current surface and/or subsurface water (*Squyres et al.*, 2004; *Knoll et al.*, 2008; *Arvidson et al.*, 2010; *Cull et al.*, 2010; *Picardi et al.*, 2005; *Feldman et al.*, 2002; *Boynton et al.*, 2002; *Mitrafanov et al.*, 2002).

The next decade is expected to witness the arrival at Mars of a number of missions launched by a variety of the world's space agencies. In September 2014, NASA's Mars Atmosphere and Volatile Evolution (MAVEN) mission is scheduled to enter orbit, with a principal objective of exploring Mars' climate history through measurements of ionospheric properties and by sampling trace materials in the upper reaches of the atmosphere to determine the rate of leakage into space, over the eons, of CO<sub>2</sub>, N<sub>2</sub>, Ar, and H<sub>2</sub>O (*Jakosky*, 2011). Other missions from Europe and Asia to search for signs of life are the Indian Mangalyaan

mission planned for launch in November 2013, and the joint ESA/Russian Federal Space Agency dual-launch mission currently planned for liftoff in 2016 and 2018. The 2016 launch will (1) deliver the Trace Gas Orbiter to globally map important minor species, in particular, gaseous methane, in the atmosphere, and (2) land the Entry, Descent and Landing Demonstrator Module (EDM) that will characterize the local dust environment. The 2018 launch will deliver a rover via a Russian-developed landing system. Meanwhile, the U.S. is set to launch the InSight surface lander mission in 2016 to investigate the planet's interior, principally via seismometry and heat flow measurements. NASA is also developing plans to launch a follow-on nuclear-powered Curiosity-style rover mission in 2020 that will continue the long-term exploration of the martian surface.

## 1.3. Future Exploration of the Origin and Early Evolution of the Terrestrial Planets

A major impetus for the continued revival of Venus exploration and a major expansion of Mars exploration — including proposed sample return missions — has come from the U.S. planetary science community. In 2003 and 2011, under the auspices of the Space Studies Board of the National Research Council, the community's Solar System Exploration Survey (SSES) produced "Decadal Surveys" summarizing and prioritizing scientific objectives and missions to the planets for the ensuing decade. A major finding of both reports (*National Research Council*, 2003, 2011) is the need for direct, *in situ* sampling of both Mars and Venus, both their atmospheres and surfaces. For Mars, many of the *in situ* rover, lander, and orbiter experiments currently being conducted are direct and valuable responses by NASA and other space agencies across the world to such community recommendations.

Extraordinary *in situ* experiments at the surface of Venus by the Venera and Vega landers in the 1970s and 1980s have provided the basis of what we know about the elementary composition of the surface (*Surkov et al.*, 1984; *Barsukov et al.*, 1986; *Barsukov*, 1992). In the same era, Pioneer Venus (*Oyama et al.*, 1980) and the Vega probes (*Krasnapolsky*, 1989) directly sampled atmospheric gases and clouds successfully above 22 km altitude. In the 1990s, fundamental new measurements were provided during the fleeting (less than a few hours) Galileo and Cassini flybys, including the first close-up near-infrared images and spectra of Venus' lower atmosphere and surface (e.g., *Carlson et al.*, 1991, 1993a,b; *Collard et al.*, 1993; *Baines et al.*, 2000; *Hashimoto et al.*, 2008). The ongoing Venus Express, in orbit since April 2006, has been sending back data nearly continuously, with over 4 terabytes of science measurements returned as of mid 2013, much of it composed of near-infrared imagery and spectra pioneered by Galileo and Cassini. The Venus Express mission is currently expected to end in 2015 upon the exhaustion of the spacecraft's fuel, needed to maintain orbit. Near that time, Akatsuki, Japan's first spacecraft to Venus, is currently planned to make a second attempt to

enter orbit, having failed on its first attempt in December 2010. Taking the reins from Venus Express, Akatsuki will continue to monitor Venus' S-based chemistry and circulation, particularly in the middle cloud layer.

Despite the successes and expectations of the flybys of the 1990s and the orbiters of the early twenty-first century, since the mid 1980s we have yet to fly experiments that provide the necessary *in situ* sampling and other measurements to answer fundamental questions dealing with the origin and evolution of Venus, including the role of the local solar nebula in creating planets inside Earth's orbit. Required measurements include those currently being conducted on Mars by SAM: the abundances and isotopic ratios of inert noble gases — in particular the heavier constituents Xe and Kr — and isotopic ratios of the light elements C, N, and O. As is the case for Mars, such measurements bear the telltale fingerprints of the planet's origin and evolution, as is well illustrated in the remainder of this chapter.

#### 1.4. Overview

In section 2, we present a general review of the state of knowledge of the origin and evolution of the trio of rocky, atmosphere-enshrouded planets Earth, Mars, and Venus. Here, we focus on what is known based on solid samples collected on Earth, including information from asteroidal and martian meteorites. Additional information comes from lunar samples.

As noted above, fundamental additional evidence comes from atmospheric samples, in particular from noble gases, their isotopes, and the isotopes of light gases. In section 3 we use Venus as a case study, examining what is known from spacecraft data of its isotopic record. We note that compared to Earth and Mars, Venus is rather poorly covered; only Ar and bulk Ne have thus far been adequately measured. No solid samples of Venus have been returned to Earth or are known in our meteorite collections, although  $\gamma$ -ray spectrometers on the Vega landers and Veneras 8, 9, and 10 measured the abundance of the radioactive isotopes of K, Th, and U (Surkov et al., 1987). The available data lead to few constraints, allowing several possible hypotheses on the origin and early evolution of the venusian atmosphere. Since the origin of Earth's atmosphere is itself poorly understood, discovering isotopic evidence that supports a unique theory for the origin and evolution of Venus' atmosphere will likely have very large implications for understanding the origin of our own atmosphere.

Section 4 describes how noble gases in planetary atmospheres systematically constrain their origins and the processes that alter relative isotope abundances. These include atmospheric loss to space, interaction with the solar wind, interactions with the surface and interior, and impacts from space. Each process alters the abundance of noble gases in the atmosphere differently, and each process imprints a unique fractionation pattern of noble-gas isotopes. Radiogenic noble-gas isotopes reflect processes that occurred over one or two half-lives of the parent species, and therefore

a suite of isotopes sensitive to different timescales can be used to probe the evolution of planetary atmospheres.

In section 5 we discuss what the totality of spacecraft and groundbased data and theoretical models say about the long-term evolution of terrestrial planetary climates. By acquiring the right kinds of data from Venus and Mars in the future, it will be possible to reconstruct the climate evolution of both these planets in comparison with Earth's. When we begin to characterize the atmospheres of planets around other stars, it will be crucial to have this general understanding of planetary climate evolution in order to understand what these data are telling us about planetary habitability.

## 2. TOWARD UNDERSTANDING PLANETARY ORIGIN AND EVOLUTION

### 2.1. Initial Formation

As byproducts of the formation of the Sun, the formation and early evolution of the inner planetary trio Venus, Earth, and Mars are thought to largely follow the development of our central star. According to the standard model of planetary formation (Wetherill, 1990), the Sun formed out of a dense interstellar molecular cloud comprised predominantly of H, He, H<sub>2</sub>O, and refractory materials (e.g., Fe, Mg-silicates and metallic Fe) that crystallized in the form of small-particle (<0.1  $\mu$ m) dust. As the cloud collapsed due to gravitational instabilities, conservation of angular momentum dictates that some 2–10% of the gas and dust maintain the bulk of the system's angular momentum by orbiting the developing Sun in a flattened disk. Within this "solar nebula," over the next  $\sim 10^5$  years collisions between dust particles created a large population ( $\sim 10^{12}$ ) (Greenberg et al., 1978) of kilometer-sized rocky planetesimals. Accretion then proceeded mainly due to mutual gravitational perturbations among these bodies, creating, in another  $\sim 10^5$  years, approximately  $10^3$  moon-sized ( $10^{25}$ – $10^{26}$  g) "planetary embryos" in the inner 3 AU or so (e.g., models of Greenberg et al., 1978). Due to further mutual gravitational interactions, over the next  $10^7$ – $10^8$  years several hundred of the planetesimals then coalesced to form the bulk of the  $1.18 \times 10^{28}$  g composing the masses of the three terrestrial planets we see today (e.g., Wetherill, 1980). In this scenario, the gaseous component of the nebula was swept away from the inner solar system by the powerful stellar winds of the pre-main-sequence T-Tauri phase of the young Sun. This occurred during the first  $\sim 3$  m.y., approximately 2 m.y. prior to the establishment of the dominant embryos of the two largest terrestrial planets, Earth and Venus, in their near-circular, low-inclination orbits (e.g., Haisch et al., 2001).

Stellar evolution models predict that the T-Tauri phase operates until the star's convective envelope is depleted, at which point the star joins the main sequence, about 12 m.y. after stellar nuclear ignition (Zahnle and Walker, 1982). As discussed in more detail in section 4.2, if the planets were formed before the end of the Sun's T-Tauri phase, their

atmospheres would have been substantially lost due to the extreme T-Tauri winds at that time. The resulting atmospheres seen today would therefore consist predominantly of outgassed volatiles from the mantle subsequent to the end of the T-Tauri phase. Since  $^{129}\text{I}$ , the parent isotope of  $^{129}\text{Xe}$ , has a half-life of 15.7 m.y., i.e., close to the duration of the T-Tauri phase, the atmosphere that accumulated after the end of the T-Tauri phase should be depleted in  $^{129}\text{I}$ -produced  $^{129}\text{Xe}$  relative to the unaltered mantle. Indeed, this is what is observed for Earth (*Allegre and Schneider, 1994*). This in turn implies that the primary atmospheres of the terrestrial planets were subjected to ultraviolet fluxes  $10^4$  times greater than today (*Zahnle and Walker, 1982*), and thus, along with dramatically enhanced escape rates, also experienced significantly increased photochemical reactions that would have dramatically altered the chemistry and compositional character of the original atmospheres.

A significant variant in the standard model is the Kyoto model (*Hayashi et al., 1985*), wherein the loss of nebular gas in the inner solar system occurs after, and not before, the final stages of terrestrial planet formation. In this gas-rich scenario, the atmosphere of Earth is predicted to be  $10^5$  more massive than the present atmosphere (*Hayashi et al., 1979*). An alternate theory to the standard model is one invoking “gaseous giant protoplanets” that form in parallel to the formation of the Sun, as a result of massive gas-dust instabilities in the solar nebula (e.g., *von Weizsäcker, 1944; Kuiper, 1951; Cameron, 1978*). In both of these scenarios, the massive primordial atmospheres of the terrestrial planets are mostly  $\text{H}_2$  with smaller (but still substantial) amounts of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

## 2.2. Clues from $^{182}\text{Hf}$ - $^{182}\text{W}$ Isotopes

Observational evidence of the timescales for Earth’s formation and early differentiation are provided by isotopic variations produced by the decay of extinct nuclides, in particular the decay of the short-lived (9-m.y. half-life) Hf isotope  $^{182}\text{Hf}$  to the W isotope  $^{182}\text{W}$  (e.g., *Harper and Jacobsen, 1996; Jacobsen, 2005; Kleine et al., 2009*). Given the affinity of Hf for O, Hf remained enriched in Earth’s silicate mantle during differentiation, in contrast to the denser, more Fe-loving W compounds that sank to the core. Thus, a relatively high value of  $^{182}\text{W}$  abundance in the crust/mantle compared to the abundance of nonradiogenic W, as observed [with more than 90% of terrestrial W going into Earth’s core during formation (*Halliday, 2000b*)], indicates that significant  $^{182}\text{W}$  was formed after core differentiation was well along, but before  $^{182}\text{Hf}$  became extinct. The short  $^{182}\text{Hf}$  decay half-life thus implies that Earth experienced early and rapid accretion and core formation that lasted just ~30m.y., with most of the accumulation occurring in ~10 m.y. (*Jacobsen, 2005*).

For Mars, W-isotopic measurements from martian meteorites indicate a significantly shorter accretion and core-formation period, perhaps as short as 15 m.y. (*Lee and Halliday, 1997; Halliday, 2001*), about one-half the rate

noted above and one-fourth as long as their own analyses for Earth. Since Mars has about one-eighth the mass of Earth, this result implies that the two planets had similar accretion rates during the Mars formation period. Noting a correlation between Th/Hf and  $^{176}\text{Hf}/^{177}\text{Hf}$  in chondrites, however, *Dauphas and Pourmand (2011)* estimated the mobility of Th in martian meteorites. This permitted a much more accurate accretion rate from the Hf/W ratio, indicating that Mars accreted to half its final size in 1.8(+9,–1) m.y., again consistent with the notion that Mars and Earth had similar accretion rates during the relatively short Mars formation period. Thus, rather than the rate of accretion, a major difference in formation between the two planets is the longer period of accretion for Earth.

Meteorites from Mars exhibit marked heterogeneities in W-isotopic abundances, which then places an upper limit on the date of the last global-scale impact on Mars. These heterogeneities are significantly larger than found on Earth, where mantle convection over the eons has smoothed Hf-W variability (*Halliday et al., 2000b*). Indeed, the earliest isotopic heterogeneities on Earth are less than 2 b.y. old, while the martian mantle heterogeneities must have occurred during the first 30 m.y. of the solar system. Thus, unlike Earth, Mars suffered no major, moon-forming impacts sufficiently energetic to effectively homogenize the isotopic W composition later than 4.53 Ga (*Lee and Halliday, 1997*). These heterogeneities also indicate that large-scale convective mantle-mixing processes, such as those that drive Earth’s plate tectonics, are absent on Mars. While the large shield constructs such as Tharsis and Elysium are indicative of some convective upwelling, there is little observational evidence for large-scale convective overturn (*Breuer et al., 1997*), and there are few if any plate-tectonic-like features (*Sleep, 1994*).

## 2.3. Evidence and Impact of Large Collisions Near the End of Planetary Formation

Many of the unique characteristics of the planets we see today are thought to result from unpredictably stochastic events near the end of their formation processes — such as the “giant impacts” of the last protoplanetary collisions likely experienced by each planet (*Kaula, 1990*). For example, the prevailing theory of lunar genesis holds that Earth’s Moon was formed from the collision of a Mars-sized object with the forming Earth some 50–70 m.y. after the start of planetary formation (e.g., *Boss, 1986; Stevenson, 1987; Newsom and Taylor, 1989; Benz et al., 1986, 1987, 1989; Cameron and Benz, 1991; Halliday, 2000a,b*) after 50–95% of Earth was accreted (*Halliday, 2000a; Canup, 2004*). A somewhat earlier date of ~30 m.y. after the start of planetary formation is reported by *Jacobsen (2005)* from analysis of Hf-W data from Apollo lunar samples.

A number of the Moon’s gross features, such as its low bulk Fe abundance, the large depletion of volatile elements, and the similarity of its overall silicate chemistry to that of Earth’s mantle, are natural consequences of the giant colli-

sion model (Hartmann, 1986; Wänke and Dreibus, 1986). This giant collision also likely created a global terrestrial magma ocean (Melosh, 1990; Benz and Cameron, 1990; Stevenson, 1987) from the melting of 30–55% of Earth (Tonks and Melosh, 1993) to a depth of ~2000 km (Canup, 2008) and, perhaps along with other major collisions, helped tear away Earth's original atmosphere (Cameron, 1983).

A persistent problem with this picture has been the similarity of O isotopes in the mantle silicates of Earth and the Moon. Impact simulations show that most of the Moon's mantle should consist of the mantle of the impactor (Canup, 2004). However, isotopic ratios of O vary smoothly with distance from the Sun, reflecting the temperature regime during silicate condensation. A large, Mars-sized impactor would have to have come from outside Earth's accretional feeding zone, and therefore should have had a different isotopic O pattern than that found in Earth's mantle (Canup, 2004). Recently, impact simulations incorporating smooth particle hydrodynamics have shown that an oblique impact by a larger impactor would have led to more mantle mixing and a thorough homogenization of mantle material, including O isotopes (Canup, 2012). This oblique impact likely gave Earth a rapid rotation rate (Cameron and Ward, 1976), subsequently altered by both tidal interactions between the Moon and Earth and an orbital resonance between the Sun and the Moon (Cuk and Stewart, 2012), that slowed Earth's spin from its initial ~4.1-hour period (e.g., Dones and Tremaine, 1993) to the 24-hour period we see today.

On Venus, the last impact by a large planetesimal is thought to be responsible for the planet's unusually slow — and retrograde — spin rate, resulting in a solar day that is equivalent to 117 Earth days between sunrises and — due to its backward spin — a sidereal day 18 days longer than its orbital period of 224.7 days. This exceedingly slow rate of rotation may be the reason why Venus does not have an intrinsic magnetic field, although Stevenson (2003) concludes that slow rotation may be more favorable for a magnetic dynamo than fast rotation. Whether due to the lack of plate tectonics (discussed below) or its spin state, Venus' lack of a magnetic field exposes the planet to the ravages of the solar wind, which has proceeded to drain it of most of its H and H<sub>2</sub>O. This turned the planet into a dry world of S-based clouds and meteorology and starved it of the lubricating and chemical effects of mantle water needed to operate major Earth-like geologic processes, such as plate tectonics, resulting in a geologic history radically different from Earth's.

## 2.4. From Oceans of Magma to Seas of Water

For all the terrestrial planets, the immense amount of gravitational energy released by accretion during planetary formation resulted in temperatures sufficiently hot to cause global melting, the differentiation of materials, and the formation of a hot, dense core. Core formation involves a positive feedback whereby the mantle is heated by the release of gravitational potential energy from the fall of Fe

and other dense materials to the center. The warmer, more fluid mantle speeds the collection of these dense materials at the core, releasing yet more potential energy (Turcotte and Schubert, 1982). Several additional mechanisms may have contributed to the trapping of heat to prolong near-surface melting to create a variety of possible magma oceans (Abe, 1997), including (1) the blanketing effect of a protoatmosphere (e.g., Abe and Matsui, 1985, 1986; Hayashi et al., 1979; Matsui and Abe, 1986; Zahnle et al., 1988), resulting in a surface ocean of magma in chemical equilibrium with the atmosphere, and (2) the deposition of underground heat by planetesimal impacts, producing a subsurface magma ocean (e.g., Safronov, 1969, 1978; Kaula, 1979; Davies, 1985; Coradini et al., 1983). As noted for the Moon-forming collision, any giant impact would likely generate a completely molten deep magma ocean (e.g., Melosh, 1990), with temperatures exceeding several thousand Kelvin over the entire Earth. Indeed, this may have happened several times to Earth during its latter stages, forming a magma ocean each time (Wetherill, 1988). A recent interpretation of Earth's Ne- and Xe-isotopic record, however, implies that these impact events never succeeded in rehomogenizing the mantle (Mukhopadhyay, 2012). Regardless, without an atmospheric blanketing effect, the deep magma ocean would be transient, cooling via radiation into space and solidifying the lower mantle within a few thousand years (Abe, 1997).

With an atmospheric blanketing effect — due to either the gravitationally captured solar-type, H<sub>2</sub>-dominated proto-atmosphere or the impact-produced steam atmosphere — a magma ocean can be sustained for ~5 m.y., as indicated by the analytical modeling of Elkins-Tanton (2008) for both Earth and Mars. These models include the effects of (1) the partitioning of H<sub>2</sub>O and CO<sub>2</sub> between mineral assemblages that accumulate in the solidifying mantle, (2) evolving liquid compositions, and (3) a growing atmosphere. Salient results are that mantle solidification is 98% complete in less than 5 m.y. for all magma oceans investigated for both planets, and is less than 100,000 years for low-volatile magma oceans. For all cases, Elkins-Tanton found that subsequent cooling to clement surface conditions occurs in 5–10 m.y.

The modeling results of Elkins-Tanton further indicate that, for both Earth and Mars, atmospheres significantly thicker than those that exist today could have been created through solidification of a magma ocean with low initial volatile content. Although Mars is relatively dry today, as much as 99% of Mars' original volatile content is thought to have been lost by 3.8 Ga through hydrodynamic escape, impacts, and sputtering by solar wind.

Direct measurements of terrestrial materials largely confirm these theoretical results, which depict a rapid evolution to clement surface conditions able to support a hydrosphere. While no rocks exist from the “dark ages” of the Hadean era 4.0–4.5 Ga (Harrison et al., 2008; Harrison, 2009) — due presumably to the late heavy bombardment ca. 3.9 Ga (Gomes et al., 2005) — detrital zircons from this period have been found in metamorphosed sediments at Jack Hills in western Australia. These hydrologically formed minerals

were created by the remelting and resolidification of ocean sediments to granite and zircon, dating variously to  $4.404 \pm 8$  Ga (Wilde *et al.*, 2001; Peck *et al.*, 2001) and  $\sim 4.36$  Ga (Harrison *et al.*, 2008). Additional evidence for their hydrologic heritage comes from two measures of temperature derived from the zircons: (1) the crystallization temperature of Ti found within the zircons, which are found clustered over a narrow range of temperatures,  $680 \pm 25^\circ\text{C}$  (Watson and Harrison, 2005, 2006), and (2) the high  $^{18}\text{O}$  content of zircons indicative of relatively cool temperatures (Valley *et al.*, 2002). Both results substantiate the conclusion that the zircons encountered wet, minimum-melting conditions during their formation. Together, these results reveal that Earth cooled rapidly enough to form both continental crust and liquid water oceans by 4.36–4.40 Ga, just  $\sim 160$ –210 m.y. after the condensation of the first solid particles in the solar system at 4.56 Ga (Valley *et al.*, 2002) and less than 140 m.y. after the Moon-forming impact (Touboul *et al.*, 2007). The crust itself may have started forming much earlier: prior to 4.5 Ga, as inferred by the crustal-type Lu/Hf environment of zircons determined by Harrison *et al.* (2008), just  $\sim 60$  m.y. after the solid-particle formation in the solar nebula. By  $\sim 4.36$  Ga, the crust had evolved to the point of taking on continental characteristics (Harrison *et al.*, 2008), including the current pattern of crust formation, erosion, and sediment recycling behavior of plate tectonics (Watson and Harrison, 2005).

Two mechanisms have been noted to explain this early appearance of a water ocean on terrestrial planets (Elkins-Tanton, 2011). First, a solidifying magma ocean may be water-enriched to the point that excess water extrudes onto the planet's surface at the end of the period of silicate mineral solidification. Second, a water ocean may form when a thick supercritical fluid and steam atmosphere collapses into a water ocean upon cooling past the critical point of water (Abe, 1997; Elkins-Tanton, 2008).

According to the analysis of Elkins-Tanton (2011), the mechanism of water extrusion from solidifying magma may occur for planets with water composing 1–3% of its bulk mass, while planets with an initial water content of 0.01% by mass or even somewhat less can form oceans hundreds of meters deep from a collapsing steam atmosphere. The Elkins-Tanton models include conditions for Earth, where the total mass of frozen and liquid water on the planet's surface today is about  $1.4 \times 10^{21}$  kg, while the mass of Earth's mantle is  $6.0 \times 10^{24}$  kg. Thus, in bulk, water in the silicate Earth is at least 0.02% by mass, or 200 ppm (Elkins-Tanton, 2008). Although there are good constraints on the water abundance of the upper mantle (Saal *et al.*, 2002), the total concentration of water in Earth's interior is poorly constrained but undoubtedly somewhat larger than 200 ppm. These models also should apply to both Venus and Mars, since they likely formed out of similar water-rich chondritic material that largely formed Earth, containing up to 20% water by mass (Wood, 2005).

These models then indicate that water oceans may have formed on Earth, Venus, and Mars early in each of their

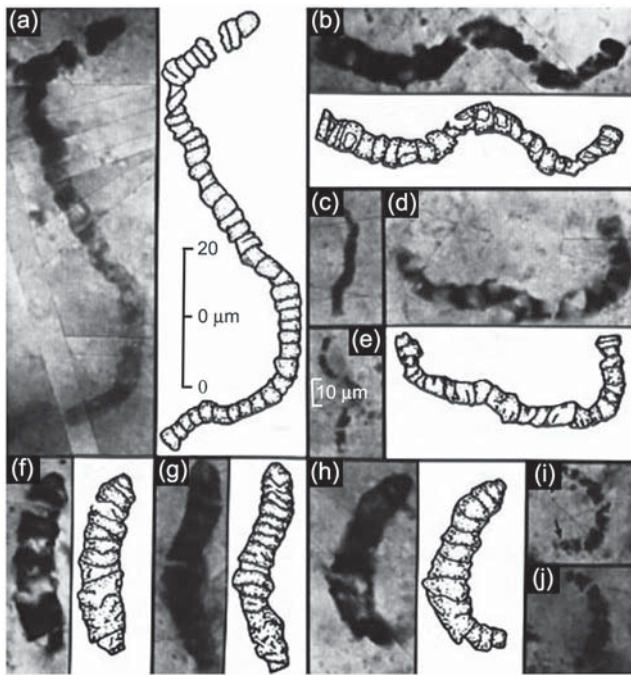
histories. Also, as noted by Elkins-Tanton (2011), water oceans may be commonplace on rocky planets throughout the universe, produced by the collapse of their steam atmospheres within tens to hundreds of millions of years of their last major accretionary impact.

As discussed in the chapter by Bullock and Grinspoon (this volume), the lifetime of such oceans is uncertain, depending on atmospheric escape mechanisms, including atmospheric erosion by stellar fluxes of ultraviolet light and charged particles, and blowoff by large residual impacts. On Earth, the late bombardment between 3.8 and 4.0 Ga — during which time the impact rate was  $10^3$  greater than today (Valley *et al.*, 2002) — may have temporarily vaporized a significant fraction of Earth's oceans. However, the constancy of the  $^{18}\text{O}/^{16}\text{O}$ -isotopic ratio found throughout the Archean (4.4–2.6 Ga) (Valley *et al.*, 2002) suggests that conditions conducive to oceans may not have been entirely eliminated from the globe during the bombardment period.

## 2.5. The Dawn of Life

The existence of liquid water around 4.4 Ga has important implications for the evolution of life (Sleep *et al.*, 2011). Ancient sediments that have undergone some metamorphism and carbonaceous materials — including carbonaceous inclusions within grains of apatite in West Greenland (Moorbath *et al.*, 1986) — 3.8 G.y. old have been found to hold distinctively biogenic C-isotope ratios (Hayes *et al.*, 1983; Schidlowski, 1988; Mojzsis *et al.*, 1996), suggesting that life arose near the conclusion of the late heavy bombardment ( $>3.8$  Ga). Microfossils as old as 3.5 Ga (Schopf, 1993) show structural complexity, indicating that photosynthetic life able to leave durable fossils may have evolved over  $\sim 0.3$  G.y. or perhaps longer (Fig. 1). Studies of ancient metasediments and their fossils are notoriously difficult, however, and both the C-isotope and microfossil records have been challenged (e.g., Brasier *et al.*, 2002). As noted by Wilde *et al.* (2001), primitive life may have arisen in ancient oceans as early as  $\sim 4.4$  Ga, but may have been globally extinguished and subsequently arose more than once by the high rate of impacts during the late heavy bombardment (Sleep and Zahnle, 1998). Alternatively, as suggested by the  $^{18}\text{O}$  analysis of Valley *et al.* (2002) for oceans, life may have survived the bombardment cataclysm. This view is consistent with the time of molecular divergence among archaeobacteria determined by Battistuzzi *et al.* (2004), which is consistent with 4.1 Ga. Thus life may have risen within 0.3 Ga after standing bodies of water appeared on Earth.

Figure 2 summarizes the current understanding of the possible eras of oceans based on the bombardment history of Earth. During periods of low bombardment, i.e., within approximately two orders of magnitude of today's rate of about one major impact every 50 m.y., conditions would be sufficiently clement to sustain oceans. Such relatively quiescent, cool, wet periods appear likely not only after the late heavy bombardment that occurred from 3.8 to 4.0 Ga,

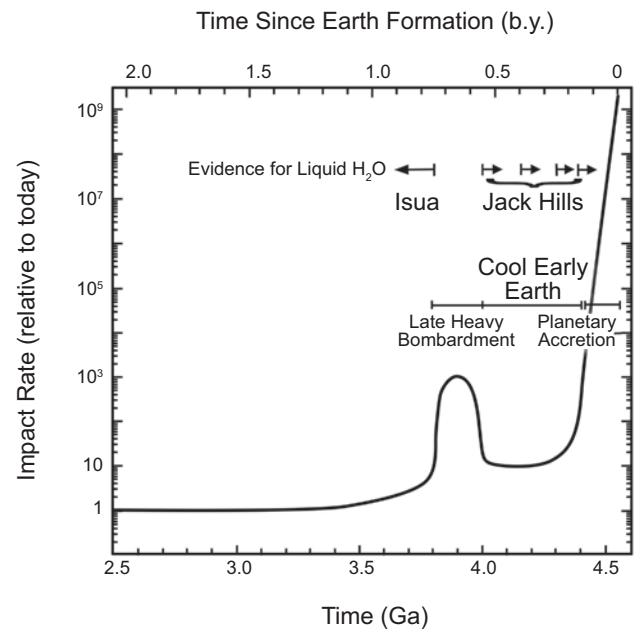


**Fig. 1.** Microfossils and interpretive drawings of the earliest life found on Earth. These carbonaceous fossils are from the Apex chert in North Pole, Australia, and are 3.465 G.y. old. These multicellular organisms were cyanobacteria and thus harnessed solar energy through photosynthesis. Fossils seen in (a), (b), (c), (d), and (e) are archaea, *Primaevifilum amoenum*; those seen in (f), (g), (h), (i), and (j) are *Primaevifilum conicoterminatum*. Adapted from *Schopf (1992)*.

but also during the ~0.4-G.y. period from 4.4 to 4.0 Ga. As noted by *Valley et al. (2002)*, it may then be a misnomer to include this 0.4-G.y. era in the Hadean (“hell-like”) period from 4.0–4.5 Ga. Indeed, given the real possibility and importance of the birth of life on Earth during this period, “The Arcadian” may be a more appropriate title.

## 2.6. Planetary Samples

Our picture of the early history of Earth and Mars is beginning to be completed in some detail, due largely to the existence of solid materials such as martian meteorites embedded with fruitful clues to their conditions of formation. The mild gravity and low atmospheric pressure of Mars favor the expulsion of surface materials into space by kilometer-sized impactors (*Melosh, 1988*). Even more fortuitously, gravitational perturbations due to Jupiter tend to steer such ejected material into Earth-crossing trajectories (*Gladman, 1997*). The process is so efficient that meteorites from Mars are in transit to Earth for an average of only 15 m.y., based on cosmic-ray-exposure ages. The isotopic



**Fig. 2.** The estimated meteorite-impact rate during the first 2 b.y. of Earth’s history, as proposed by *Valley et al. (2002)*. The cool early Earth hypothesis of *Valley et al.* indicates that the meteoritic flux dropped precipitously over the ~0.15-G.y. period of accretion, so that by 4.3 Ga, Earth was cool enough to support liquid water. Evidence for clement conditions during this era before the late heavy bombardment at ~3.9 Ga comes from the analysis of  $^{18}\text{O}$  in zircon samples. Post late heavy bombardment, “Isua” denotes the oldest known water-lain chemical sediments, found in the Isua supracrustal belt in western Greenland, dating to 3.6–3.85 Ga (*Nutmans et al., 1997; Whitehouse et al., 1999*). Adapted from *Valley et al. (2002)*.

ratios of gases captured within glassy inclusions of these meteorites match the atmosphere of Mars precisely, as measured by the Viking landers (*Clark et al., 1976*). These samples from our neighboring planet have taught us much about the petrology and mineralogy of martian rocks, as well as about processes that have altered them since they were formed.

Venus, for which we have no known solid samples in hand, is more poorly constrained. The extreme conditions of its surface — with temperatures exceeding 470°C and pressures greater than 94 bar — together with its significant gravity (surface gravity ~90% of Earth) prevent the ready return of rock samples via surface lander missions. In addition, we know of no Venus rocks in our meteorite collections. Thus, to paint the picture of Venus’ early history, we are left with the analysis of its bulk properties — including its lack of both a moon and a magnetic field, and the unusually slow speed and retrograde direction of its rotation — and with the interpretation of atmospheric samples acquired by planetary probes, all of which, of course, aid in our understanding of Earth and Mars as well.

### 3. THE EARLY EVOLUTION OF VENUS: EVIDENCE FROM BULK PROPERTIES AND RADAR IMAGERY

Venus and Earth differ by less than 20% in their size, mass, and bulk density and are at comparable distances from the Sun, suggesting that these two planets had similar early histories of accretion and internal differentiation. Nevertheless, Venus and Earth proceeded along different evolutionary paths, as is evident from a comparison of the planets' satellites (*Alemi and Stevenson, 2006*), magnetic fields (*Nimmo and Stevenson, 2000*), tectonics (*Solomon et al., 1992*), rotational states (*Del Genio and Suozzo, 1987*), and atmospheres (*Kasting, 1988*).

#### 3.1. Natural Satellites

For reasons that are poorly understood, Venus lacks a moon. This could simply be by chance, of course, but as noted earlier, Venus was likely subject to major impacts in its early evolution comparable to Earth's Moon-forming impact. The lack of a venusian moon has been attributed to the inward spiraling of a previously existing satellite that eventually collided with the planet. Satellite escape is another possible explanation (*Stevenson, 2006*). However, neither hypothesis is particularly plausible. The inward-spiraling scenario is unlikely to produce Venus' retrograde motion, since such a satellite would likely have been in a prograde orbit. The escape scenario is unlikely for reasonable  $Q$  values and satellite masses (*Stevenson, 2006*).

#### 3.2. Planetary Magnetic Field

Today, Venus lacks an intrinsic magnetic field (*Russell, 1980; Phillips and Russell, 1987; Donahue and Russell, 1997; Nimmo, 2002*), as may reasonably be explained through an analysis of the planet's thermal evolution. Like Earth, Venus was probably initially hot and differentiated, and thus also probably had a liquid metallic core that, to some extent, likely still exists today. An indication that at least some portion of Venus' core is currently still liquid is provided by the tidal Love number,  $0.295 \pm 0.066$ , determined from Doppler radio tracking of Magellan and Pioneer Venus (*Konopliv and Yoder, 1996; Sjogren et al., 1997; Yoder, 1997*). Hence it is quite possible that the planet had an early dynamo-generated magnetic field that later disappeared, its lifetime dependent upon the cooling history of the core. In particular, for a magnetic field to exist, the rate of core cooling, controlled by the mantle's ability to extract heat from the core, must have been strong enough to support convection and dynamo action in the core. One explanation then for the lack of a magnetic field today is that Venus underwent a transition in the efficiency of the core to transfer heat, as has been proposed as the explanation for the lack of a martian magnetic field (*Nimmo and Stevenson, 2000*). Venus potentially evolved from efficient core cooling by a plate-tectonic-like style of mantle convection to an inefficient style

of stagnant or sluggish lid mantle convection that cooled the core slower than required to support dynamo activity. One potential proof of the existence of an ancient dynamo would be the detection of remanent magnetization from this epoch. However, since Venus' high surface temperature is close to the Curie point of most natural ferromagnetic minerals, it seems unlikely that surface materials could have retained such evidence over the eons.

A second explanation for the lack of a magnetic field is also related to inefficient core cooling by the mantle and the lower pressure in Venus' core compared with the pressure in Earth's core due to Venus' smaller mass. It is believed that dynamo action in Earth's core is substantially facilitated by compositional convection driven by inner core solidification and growth. On Venus, it is possible that the core has not yet cooled sufficiently to initiate such inner core growth, but has cooled enough to prevent the operation of a purely thermally driven dynamo (*Stevenson et al., 1983*).

#### 3.3. Radar Imaging of Venus' Surface

Radar global imagery by Magellan strongly indicates that Venus is a one-plate planet, devoid of plate tectonics, as suggested by the almost total absence of a global system of ridges and trenches as found in Earth's oceans (*Kaula and Phillips, 1981*). Mantle convection in Venus must therefore be of the sluggish or stagnant lid mode, which, as noted earlier, is a relatively inefficient way to cool the core (*Schubert et al., 1997*). The absence of plate tectonics and its style of mantle convection could be directly related to the lack of water on Venus (*Sleep, 2000*). It is widely understood that the asthenosphere, the ductile layer of the upper mantle just below the lithosphere, serves to lubricate plate motion on Earth and facilitate plate tectonics. The physical properties of this layer are due to its water content (*Turcotte and Schubert, 1988*). It is therefore possible that atmospheric evolution, by way of an intense greenhouse effect and runaway loss of water (Bullock and Grinspoon, this volume), had a controlling influence on the evolution of the entire solid planet, shutting down plate tectonics, core cooling, dynamo action and a magnetic field. Thus a relatively minor part of Venus by mass — the atmosphere — could have controlled the thermal and rotational history of the entire planet.

Venus rotates in a retrograde sense with a planetary spin period of 243 Earth days, more than 236 times that of Mars and 335 times longer than any of the gas/ice giant planets. As discussed earlier, how this state of slow retrograde spin came about is unknown, but it might be maintained by a balance between solid body tides raised by the Sun's gravity and a frictional torque on the solid planet exerted by the superrotating atmosphere (*Gold and Soter, 1969, 1979; Kundt, 1977; Ingersoll and Dobrovolskis, 1978; Dobrovolskis and Ingersoll, 1980*). Such a balance invokes the solar torque on the atmospheric thermal tide as the source of atmospheric angular momentum. Alternatively, the angular momentum of the superrotating atmosphere, some  $1.6 \times 10^{-3}$  of the



solid-body angular momentum (Schubert, 1983), could be derived from the solid planet, resulting in a secular variation in the planet's spin. Recent groundbased high-precision long-baseline radar has detected length-of-day variations of 50 ppm over ~8 years (Margot et al., 2012), thus confirming that such an angular momentum exchange likely plays a meaningful role in powering the superrotation of Venus' atmosphere.

### 3.4. Atmospheric Evolution

Today, the composition and structure of the atmosphere of Earth bears little resemblance to that of Venus or Mars (see Table 1 for a comparison of the atmospheric compositions of the terrestrial planets). For example, the venusian atmosphere is almost 100 times as massive as Earth's, which in turn is nearly 100 times more massive than Mars. Also, while N is the dominant gas in Earth's atmosphere, composing some 78% of the atmosphere by volume, it composes less than 4% of the content of both Venus and Mars. Indeed, N was recently found to be less abundant on Mars than the noble element Ar (volume mixing ratio of 0.0193 for  $^{40}\text{Ar}$  vs. 0.0189 for  $\text{N}_2$ ) (Mahaffy et al., 2013).

As this last result indicates, since arriving at Mars in August 2012, the SAM instrument on the Mars Science Laboratory (MSL) Curiosity rover has been fundamentally refining our understanding of the composition of the martian atmosphere. Besides finding the surprisingly large  $^{40}\text{Ar}$  abundance, SAM has found a  $^{40}\text{Ar}/\text{N}_2$  ratio that is nearly a factor of two greater than that measured by Viking (Mahaffy et al., 2013). Considering the noncondensable and inert nature of these volatiles, their ratio is not expected to change with time or seasons, thus implying an unrecognized instrumental effect or unknown atmospheric process (Atreya et al., 2013). Very similar values of the  $^{13}\text{C}$  isotope are obtained by the quadrupole mass spectrometer (QMS) and the tunable laser spectrometer (TLS) subsystems on SAM, namely,  $\delta^{13}\text{C}$  of 45‰ (Mahaffy et al., 2013), whereas for the O-isotope  $^{18}\text{O}$ , the TLS measures  $\delta^{18}\text{O}$  of 48‰ in  $\text{CO}_2$  (Webster et al., 2013a). These C and O fractionations showing enhancement in the heavy isotopes imply loss of a substantial fraction of the original atmosphere from Mars due to escape processes. Similarly, loss of a substantial amount of water from Mars is implied by the TLS measurement of an enhanced D component, with a  $\delta\text{D}$  of 5000‰ (Webster et al., 2013a). The isotopic fractionation carries the geologic and climate history of all terrestrial planets, as discussed in sections 4 and 5.

Another significant result of the initial SAM measurements is the lack of methane in the atmosphere of Mars. As methane is a potential biomarker — 90–95% of the methane in Earth's atmosphere is biologically derived — and since previous Mars orbital and groundbased observations indicated 10–70 ppbv of the gas in the atmosphere (Formisano et al., 2004; Mumma et al., 2009), the *in situ* SAM measurements were eagerly anticipated. Somewhat surprisingly, the highly precise TLS measurements obtained at the surface

of Mars found no evidence of methane, with an upper limit of 3 ppbv (Webster et al., 2013b). If methane were present at such low levels, it could result from any combination of processes, including (1) near-surface-rock reactions such as serpentinization, followed by metal-catalyzed Fischer-Tropsch reactions; (2) ultraviolet/charged particle degradation of surface organics; or (3) methanogenesis (Atreya et al., 2007, 2011).

In contrast to the thin, cold atmosphere of Mars (average surface pressure and temperature of 6 mbar and 218 K), and Earth's habitable ground-level conditions (1 bar and 288 K surface pressure and temperature, respectively), the surface environment of Venus is extreme: about 94 bar and 740 K (Seiff, 1983). Venus' relatively thick atmosphere is predominantly  $\text{CO}_2$ , roughly equivalent to the amount of  $\text{CO}_2$  tied up in carbonate rocks on Earth. Also, the total amount of water in Venus' atmosphere is within about an order of magnitude of the total water content of Earth's atmosphere, but is spread over a column number density of gas that is nearly two orders of magnitude greater. Thus the atmosphere of Venus is extremely dry, with a  $\text{H}_2\text{O}$  volume mixing ratio of about 30 ppm, corresponding to  $\sim 10^{-3}$  of the molar fraction of water found in Earth's atmosphere — and several orders of magnitude less if Earth's oceans are included. Consequently, Venus' ubiquitous cloud system is composed not of water, but of sulfuric acid, indicative of a complex cycle of S-based corrosive chemistry throughout the atmosphere. How did the atmosphere evolve to its present state if it was initially similar to Earth's atmosphere with a substantial complement of water? As noted in Bullock and Grinspoon (this volume), a strong possibility is that an intense greenhouse effect led to the vaporization of all water on early Venus, followed by photodissociation of the water vapor at high altitudes and the escape of the released H into space. Without liquid water on its surface,  $\text{CO}_2$  could then not be sequestered in the surface rocks. This change in Venus' atmosphere, if it occurred, would have triggered changes in the planet reaching all the way to its core. As noted earlier, the loss of water would have stopped plate tectonics. This would have changed the style of mantle convection, slowed the rate of core cooling, and turned off the magnetic field.

How can these evolutionary story lines be checked? As discussed in detail below, one way is the measurement of noble gases, their isotopic compositions, and the isotopic compositions of light elements measured in planetary atmospheres.

## 4. NOBLE GASES: THE KEY TO THE PAST

### 4.1. The Significance of Atmospheric Noble Gases

The earliest record of the atmospheres of the terrestrial planets is contained in the noble gases and their isotopes. This is because these elements do not react with the surface or with other gases, and isotopic fractionation records cataclysmic events (such as collisions with planetesimals or

TABLE 1. Atmospheric compositions of the terrestrial planets.

Constituent	Primary Diagnostics	Venus	Earth	Mars
<i>Noble-Gas Abundance (VMR)</i>				
<sup>132</sup> Xe	Planetary origin: Atmospheric blow-offs Cometary/planetesimal impacts	Not measured; expected: $\sim 1.9 \times 10^{-9}$ [a,b]	$8.7 \times 10^{-8}$	$8.0 \times 10^{-8}$ [c]
<sup>84</sup> Kr	Planetary origin: Role of cold comets	$(7.0 \pm 3.5) \times 10^{-7}$ (Venera)[d] or $(5.0 \pm 2.5) \times 10^{-8}$ (PV)[d]	$1.14 \times 10^{-6}$	$3 \times 10^{-7}$ [c]
<sup>36+38</sup> Ar	Planetary origin: Roles of comets and planetesimals	$\sim (7.5 \pm 3.5) \times 10^{-5}$ [f]	$3.7 \times 10^{-5}$ [g]	$5.3 \times 10^{-6}$ [c]
<sup>40</sup> Ar	Evolution: Interior outgassing	$(7 \pm 2.5) \times 10^{-5}$ [d]	0.0093	$0.0193 \pm 0.0002$ [sam]
<sup>20</sup> Ne	Planetary origin: Common origin of Venus, Earth, Mars?	$(7 \pm 3) \times 10^{-6}$ [d]	$1.82 \times 10^{-5}$	$2.5 \times 10^{-6}$ [c]
<sup>4</sup> He	Evolution: Interior outgassing	$[1.2 (+2.4, -0.8)] \times 10^{-5}$ [d]	$5.24 \times 10^{-6}$	$(1.1 \pm 0.4) \times 10^{-6}$ [h]
<i>Noble-Gas Isotopic Ratio</i>				
<sup>129</sup> Xe/ <sup>132</sup> Xe	Early evolution: Large atmospheric blow-off	Not measured; expected: $\sim 3$	$0.983 \pm 0.001$ [j]	$2.5(+2, -1)$ [k]
<sup>136</sup> Xe/ <sup>132</sup> Xe	Origin/evolution: U–Xe hypothesis	Not measured; expected: $\sim 1$	$0.3294 \pm 0.0004$ [i]	Not measured
<sup>40</sup> Ar/ <sup>36</sup> Ar	Early history: Interior outgassing	$1.03 \pm 0.04$ [l] or $1.19 \pm 0.07$ [m]	$298.56 \pm 0.31$ [g]	$1.9 (\pm 0.3) \times 10^3$ [sam]
<sup>36</sup> Ar/ <sup>38</sup> Ar	Late formation: Large impact	$5.6 \pm 0.6$ [l] or $5.08 \pm 0.05$ [n]	$5.304$ [g]	$5.5 \pm 1.5$ [k]
<sup>21</sup> Ne/ <sup>22</sup> Ne	Origins: Common planet origin hypothesis	Not measured; expected: $< 0.067$	0.029	Not measured
<sup>20</sup> Ne/ <sup>22</sup> Ne	Early evolution: Hydrodynamic escape	$11.8 \pm 0.7$ [a]	9.78	Not measured
<sup>3</sup> He/ <sup>4</sup> He	Early evolution: Impact of solar wind	Not measured; expected: $< 3 \times 10^{-4}$ [d]	$1.37 \times 10^{-6}$	Not measured
<i>Light-Element Isotopic Ratio</i>				
D/H	Evolution: Loss of H/water	$0.016 \pm 0.002$ [p] $0.064\text{--}0.08$ above 70 km alt.[q]	$1.56 \times 10^{-4}$	$(9.3 \pm 2.2) \times 10^{-4}$ [sam]
<sup>14</sup> N/ <sup>15</sup> N	Evolution: Atmospheric loss since planetary formation	$273 (+70, -46)$ [r]	272	$170 \pm 15$ [k]
<sup>16</sup> O/ <sup>17</sup> O	Origin: Common kinship of terrestrial planets	Not measured	2520	$2577 \pm 12$ [sam]
<sup>16</sup> O/ <sup>18</sup> O	Origin: Common kinship of terrestrial planets	$500 \pm 25$ [l]	489	$462 \pm 2.5$ [sam]
<sup>33</sup> S/ <sup>32</sup> S	Past/current volcanic activity, magmatic composition	Not measured; expected: $\sim 8 \times 10^{-3}$	$8.01 \times 10^{-3}$	Not measured
<sup>34</sup> S/ <sup>32</sup> S	Past/current volcanic activity, magmatic composition	Not measured; expected: $\sim 0.04$	0.045	Not measured
<sup>12</sup> C/ <sup>13</sup> C	Biological marker	$88 (+2, -1)$ [n]	89 (inorganic)	$85.1 \pm 0.3$ [sam]
CO <sub>2</sub>	Dominant original atmospheric constituent	$0.965 \pm 0.08$ [d]	$3.9 \times 10^{-4}$	$0.9597$ [sam]
N <sub>2</sub>	Second most prevalent original atmospheric constituent	$0.035 \pm 0.08$ [d]	0.78	$0.0189 \pm 0.0004$ [sam]
O <sub>2</sub>	Disequilibrium species; indicator of biology	$< 1 \times 10^{-6}$ @60 km alt. $4 \times 10^{-5}$ @50 km $1.6 \times 10^{-5}$ near surface[d,s]	0.21	$0.00146 \pm 0.00001$ [sam]
<i>Bulk Abundances (VMR)</i>				
CO	Venus: Hot thermochemistry Tracer of meridional circulation	$2.5 \times 10^{-5}$ @35 km alt. $(3\text{--}20) \times 10^{-5}$ @60–150 km alt.[d,s]	$1.9 \times 10^{-7}$	$5.57 (\pm 0.01) \times 10^{-4}$ [sam]
H <sub>2</sub> O	Geologic styles; Earth, Venus: Condensable Earth: Weather cycle	$(4.4 \pm 0.9) \times 10^{-5}$ @0–40 km $2 \times 10^{-4}$ @50 km $1 \times 10^{-6}$ @60 km[d,s]	$4 \times 10^{-3}$ avg. 0.01–0.04 near surface	$2 \times 10^{-4}$ (seas. var.)[t]
H <sub>2</sub>	Photochemistry	$(2.5 \pm 1.0) \times 10^{-6}$ at 50–60 km[s]	$5.5 \times 10^{-7}$	$(1.5 \pm 0.5) \times 10^{-5}$ [v]
H <sub>2</sub> O <sub>2</sub>	Photochemistry	None detected	$(0.1\text{--}6) \times 10^{-8}$	$4 \times 10^{-8}$ max (seas. var.)[w]
O <sub>3</sub>	Photochemistry	None detected	$(0\text{--}7) \times 10^{-8}$	$(1\text{--}80) \times 10^{-8}$ (seas. var.)[x,sam]
CH <sub>4</sub>	Disequilibrium species; biological marker	None detected	$1.81 \times 10^{-6}$	$< 3 \times 10^{-9}$ [sam]

Data sources: [a] Donahue (1986); [b] Pepin (1991); [c] Owen et al. (1977); [d] von Zahn et al. (1983), recommended values; [f] derived from von Zahn et al. (1983) values; [g] Lee et al. (2006); [h] Krasnopolsky et al. (1994); [j] Ozima et al. (1983); [k] Owen et al. (1977), Owen (1992); [l] Hoffman et al. (1980); [m] Istomin et al. (1980a); [n] Istomin et al. (1980b); [p] Donahue et al. (1982); [q] Bertaux et al. (2007); [r] Hoffman et al. (1979); [s] Svedhem et al. (2010); [t] Smith (2002); [v] Krasnopolsky and Feldman (2001); [w] Encrenaz et al. (2004); [x] Barth (1974); [sam] Mahaffy et al. (2013), Webster et al. (2013a,b), Atreya et al. (2013).

solar-induced blow-off of the atmosphere) and geologic upheavals that degas the interior. Therefore, noble-gas isotopes in the atmosphere can point to past and present-day geologic activity (Pepin, 1991). The noble-gas elements Xe, Kr, Ar, and Ne and their isotopes provide an accessible historical record of ancient events, pertinent to planetary formation and early evolutionary processes. Radiogenic isotopes of He, Ar, and Xe also provide dating constraints on geologic processes that over the eons may have delivered materials from the deep interior to the surface (Zahnle, 1993).

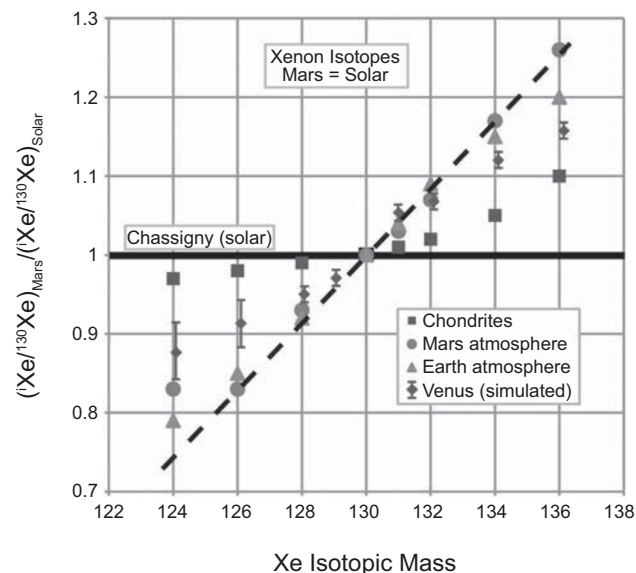
The remarkable property that renders the noble gases and their isotopes so valuable in determining ancient events is their stability against chemical alterations. Unfortunately, this stability against chemical reactions manifests itself as well in very weak coupling to electromagnetic radiation. Thus no strong spectral features exist. Consequently, the abundances of these elements cannot be readily assessed by remote sensing techniques, such as those used by Venus Express and the Mars Reconnaissance Orbiter. Only *in situ* sampling can do this. How the terrestrial planets originated and initially formed, the nature of cataclysmic events in their early histories, and insights into major geologic events throughout their evolution are examples of fundamental insights potentially provided through accurate measurements of noble gases and their isotopes. The record for Earth and Mars, particularly given the new SAM measurements, is quite complete. What is missing to complete the broad history of planetary atmospheres throughout the inner solar system are accurate measurements for Venus.

#### 4.2. Xenon and Krypton: Coded Messages of Ancient Cataclysms on Nascent Planets

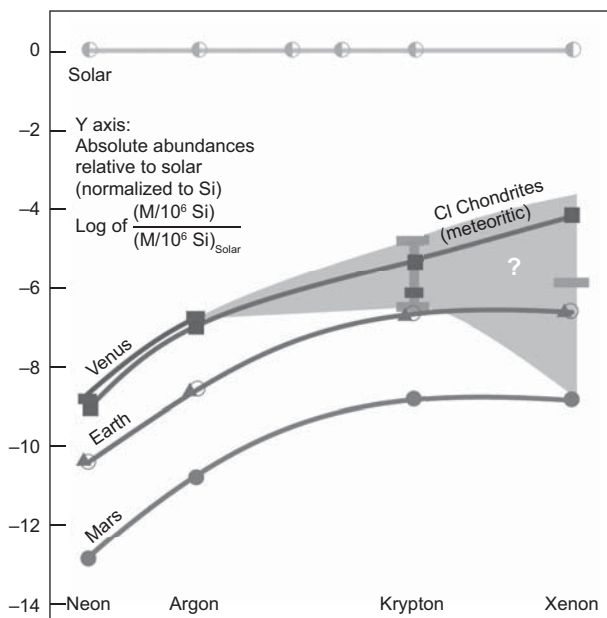
Xenon, which has never been measured on Venus, is of special interest because of its role in understanding the formation and evolution of early atmospheres on all three inner planets. On both Earth and Mars, its abundance and isotopic distribution bear little resemblance to any known source material in the solar system, which points to major globe-changing events in the early histories of both planets. As shown in Fig. 3, one difference is that on Earth and Mars, the eight nonradiogenic (primordial) isotopes of Xe are strongly mass fractionated (with a gradient of  $\sim 4\%$ /amu) compared to the solar wind or any plausible solar system source such as chondrites (Pepin, 1991; Zahnle, 1993). Another difference is that the bulk abundance of Xe on Earth and Mars is depleted with respect to Kr by a factor of  $\sim 20$  when compared to typical chondritic meteorites (Pepin, 1991), as depicted in Fig. 4 (blue and red curves vs. brown curve). As discussed below, Kr may have been preferentially released from the interiors of Earth and Mars over the eons, or it may not have been severely affected by solar-wind-induced erosional processes. In either case, the strong mass fractionation of Xe observed on Earth and Mars implies that nonradiogenic Xe isotopes are remnants of atmospheric escape that occurred during the formation of Earth and Mars.

A similar story is evident for the radiogenic isotopes of Xe, which are also markedly depleted compared to the measured abundances of their radioactive parents in primitive solar system materials. Thus, all three Xe abundance characteristics — the fractionation of primordial Xe, and the low abundances of both bulk and radiogenic Xe — indicate that one or more significant cataclysmic events on both Earth and Mars occurred late in the planetary formation process (Pepin, 2000).

The decay of short-lived isotopes of I ( $^{129}\text{I}$ , half-life 15.7 m.y.) and Pu ( $^{244}\text{Pu}$ , half-life 82 m.y.) are significant sources of radiogenic Xe. Iodine produces just a single isotope,  $^{129}\text{Xe}$ , thus enabling straightforward measurement of I-decay-produced Xe. For both Earth and Venus, the atmospheric  $^{29}\text{Xe}$  abundance is much less than expected if escape had not occurred. More specifically, Earth's atmosphere has retained only  $\sim 0.8\%$  of the complement of  $^{129}\text{Xe}$  produced by the decay of I, while today Mars has just 0.1% (Porcelli and Pepin, 2000; Ozima and Podosek, 2002). In other words, Earth and Mars have lost more than 99% of the  $^{129}\text{Xe}$  produced from the radioactive decay of I. Given the relatively short 15.7-m.y. half-life of  $^{129}\text{I}$ , much of this escape must have occurred within planetesimals during accretion. But its half-life is also long enough that much of it must have also been lost after Earth and Mars were planets, and, in the case of Earth, some of it must have been lost after the Moon-forming impact. Thus multiple impacts



**Fig. 3.** See Plate 1 for color version. Fractionation of Xe isotopes. Possible Venus Xe fractionation pattern observed by a future *in situ* mission is depicted (green) compared to the patterns of Earth, Mars, chondrites, and the Sun (after Bogard et al., 2001). A common Venus/Earth/Mars pattern would bolster the hypothesis that a common source of comets or large planetesimals delivered volatiles throughout the inner solar system. A different pattern for Venus would strengthen the solar EUV blowoff theory.



**Fig. 4.** See Plate 2 for color version. Noble gas abundances for Earth, Mars, Venus, chondrites, and the Sun (after *Pepin*, 1991). Missing Xe and poorly constrained Kr data for Venus are critical for understanding the history of its early atmosphere. For Ne and Ar, and likely Kr, Venus is more enhanced in noble gases vs. Earth and Mars, likely indicating (1) a large blowoff of the original atmospheres of Mars and Earth, and/or (2) enhanced delivery of noble elements to Venus from comets and/or solar-wind-implanted planetesimals. For Venus, the unknown/poorly constrained Xe/Kr and Kr/Ar ratios — denoted by the range of slopes of the aqua area — are consistent with all solar system objects shown, including (1) a solar-type (Jupiter and cometary) composition (orange line), (2) a chondritic composition (brown line), and (3) the composition of Earth and Mars (blue and red lines).

or other escape events — such as energized by the T-Tauri phase of the Sun — are indicated for Earth, spread over perhaps ~100 m.y. As discussed earlier in section 2.1, if the planets formed before the end of the T-Tauri phase, then the dominant escape process was likely atmospheric blow-off due to the strong T-Tauri solar wind. This would explain the enrichment of  $^{129}\text{Xe}$  in Earth's mantle compared with the atmosphere (*Allegre and Schneider*, 1994). For Venus,  $^{129}\text{Xe}$  measurements would indicate whether it also lost much of its original atmosphere during its first ~100 m.y.

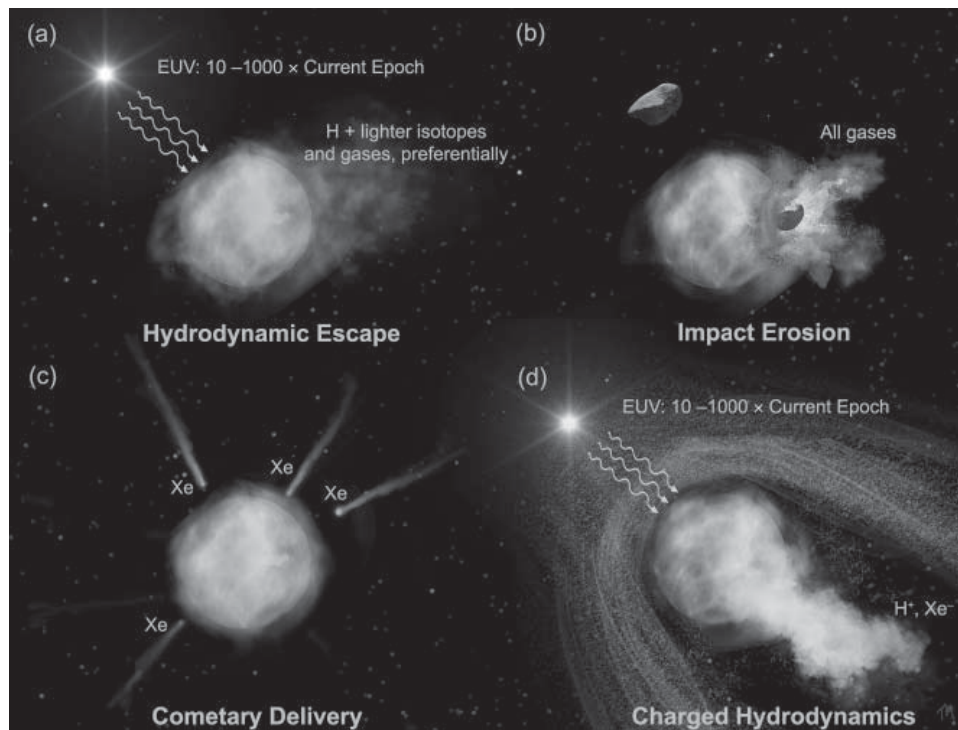
The spontaneous fission of  $^{244}\text{Pu}$  provides somewhat similar insights. Plutonium is especially noteworthy because its 82-m.y. half-life probes the early evolution of the planets for ~200 m.y. after accretion. Fission Xe has been detected both in Earth's mantle and likely in its atmosphere (*Pepin*, 2000). The precise amount is somewhat uncertain, but the upper limit is just 20% of what should have been generated by Earth's primordial Pu. The uncertain process that

removed fissionogenic Xe from the atmosphere (or perhaps kept it sequestered in the interior, preventing its venting into the atmosphere) occurred some 200 m.y. after the formation of Earth.

Four general scenarios can be invoked to explain the loss and fractionation of Xe, as illustrated schematically in Fig. 5. In one scenario, illustrated in Fig. 5a, the terrestrial planets experienced different degrees of blowoff of atmospheric H, driven by solar extreme ultraviolet (EUV) radiation more than 100 times stronger than today (*Zahnle and Walker*, 1982). As H escaped, it dragged other gases with it, the lighter gases preferentially. What stayed behind was isotopically heavy, as observed today (*Zahnle and Kasting*, 1986; *Hunten et al.*, 1987; *Sasaki and Nakazawa*, 1988; *Zahnle et al.*, 1990a; *Pepin*, 1991). A variant attributes escape to the Moon-forming impact (*Pepin*, 1997). In both of *Pepin's* (1991, 1997) models, escape was followed by degassing of the lighter noble gases from the interior — in particular Kr but not Xe, due to its stronger affinity for mantle melts than the lighter noble gases. Thus Earth's atmosphere was replenished with the amounts of lighter noble gases seen today, resulting in a relative depletion of atmospheric Xe. In both models there is relatively little escape from Venus with its much thicker atmosphere, so that Venus holds a larger and less altered portion of its original complement of noble gases.

A related model invokes impacts during accretion as the cause of the loss of atmospheric Xe (*Zahnle*, 1993) (Fig. 5b). Impact erosion is expected to expel all gases equally, regardless of mass. Thus, due to the sequestration of condensibles in the lower reaches of planetary atmospheres, any fractionation would occur between gases and condensed materials rather than among gases of different molecular mass. Consequently, one expects impact erosion to expel well-mixed noble gases much more efficiently than water sequestered in oceans or as vapor in the lower atmosphere. This, then, may have been the means by which planets lost their radiogenic Xe without losing an ocean of water. But impact erosion cannot account for the mass fractionation of the Xe isotopes. Thus, impact erosion is not the whole story, although this process may have contributed to the loss of bulk Xe.

A third scenario posits that Earth's current Xe-isotopic pattern is largely that of an external source such as large planetesimals or large comets formed in the outer solar system (Fig. 5c). Large planetesimals can fractionate isotopes by gravitational segregation (*Ozima and Podosek*, 2002; *Zahnle et al.*, 1990b). Extremely porous cold bodies, such as large comets, immersed in the cold nebular gas cloud in the outer reaches of the solar system could perhaps incorporate Xe-isotopic signatures that differ substantially from those in the inner nebula. Such bodies could then deliver these signatures to Earth (and likely other nearby bodies) to produce the puzzling distribution of Xe isotopes observed on our world today. To account for the depletions of bulk and radiogenic Xe, this hypothesis also requires that much of Earth's primordial Xe — including radiogenic products from Pu and I decay — remain sequestered deep inside the planet.



**Fig. 5.** See Plate 3 for color version. Schematics showing major features of the four main hypotheses of early planetary evolution that led to atmospheric Xe-isotopic abundances on the terrestrial planets. **(a)** Hydrodynamic escape. Early solar EUV was 100–1000 times more intense than today, heating the atmosphere to the point where H began to flow out of the exosphere. It dragged lighter molecules with it, fractionating the atmosphere so that it was isotopically heavier. **(b)** Impact erosion. Small impacts both added material and eroded the atmosphere. Large impacts blew off most of the atmosphere above the plane of impact, indiscriminate of mass, so no fractionation occurred. **(c)** Cometary delivery. Cold comets from the outer solar system with trapped Xe incorporating the isotopic ratios of the cold outer solar system impacted the surface. **(d)** Charged hydrodynamics. Hydrogen and Xe are both easily ionized, unlike other molecules. Thus ionization by the UV or solar wind preferentially allowed H and Xe to escape, while also allowing somewhat smaller portions of other ionized atoms and molecules to go along for the ride. The process is fractionating, dependent upon both mass and ionization energy.

A fourth hypothesis invokes a unique property of Xe. Unlike the other noble gases, Xe ionizes more easily than H. Consequently, when embedded in a partially ionized H wind that is flowing upward to space, Xe tends to ionize while the other noble gases remain neutral. The Coulomb force between Xe ions and protons is large and thus Xe ions are relatively easily dragged away by the escaping wind, while the lighter noble gases, being neutral, remain behind (Fig. 5d). This describes a variant on atmospheric blowoff that leaves the bulk of the atmosphere intact while allowing Xe to preferentially escape (Zahnle, 1993).

Sampling Xe and its isotopes on Venus can help resolve which mechanism or combination of mechanisms are responsible for the similar Xe-isotopic patterns found on Earth and Mars (cf. Fig. 3), thus providing key insights into the early histories of all three planets. A common fractionation signature on all three planets would indicate

a common source of Xe isotopes, strengthening the hypothesis that large comets or planetesimals were a prime source of volatiles throughout the inner solar system (Zahnle, 1993). Alternatively, due to the difference in the power of H blowoff between Venus and the outermost inner planets, the solar EUV blowoff theory would be bolstered if the Xe-isotopic fractionation pattern on Venus were found to be different than that found for Earth and Mars. The Earth-blowoff theory would be further strengthened if relatively large amounts of radiogenic  $^{129}\text{Xe}$  were found on Venus, rather than the small amounts found on Earth. This would indicate that (1) blowoff almost completely stripped Earth's atmosphere early in its history, and (2) impact erosion was relatively unimportant on Venus.

The bulk ratios of the heavy noble gases provide additional clues about the source of the materials that formed the inner planets. The Galileo probe's discovery of a uniform

enhancement of Xe, Kr, and Ar in Jupiter (Niemann *et al.*, 1998; Atreya *et al.*, 2003) implies that “solar composition” planetesimals (“cold comets”) were abundant in the solar system and compose a significant fraction of the giant planets. Krypton/xenon and Ar/Kr on Venus thus provide tests on whether these solar-like planetesimals also reached Venus in significant numbers. However, as depicted in Fig. 4, existing Kr measurements for Venus differ by more than an order of magnitude (Von Zahn *et al.*, 1983). If the lower estimate is correct, then Ar/Kr on Venus more closely resembles Jupiter’s atmosphere and the solar wind, which strengthens the cold comet hypothesis (lower boundary between Ar and Kr in Fig. 4). If the higher estimate is correct, then, as depicted by the high boundary of the aqua area between Ar and Kr in Fig. 4, the Venus Ar/Kr ratio instead resembles other objects, including meteorites, Earth, and Mars (i.e., the “planetary pattern”) as well as laboratory measurements of gases trapped in cold ice (Notesco *et al.*, 2003). The measured Kr/Xe ratio can then be invoked to help discriminate between the different sources and events that formed the inner planets. For Earth’s mantle, Holland *et al.* (2006) note that processes unique to Earth determine the abundance of Ar, Kr, and Xe. Seawater subduction controls the composition of heavy noble gases of the mantle, so direct bulk comparisons of these gases from the interiors of the planets is likely to be difficult. For planetary atmospheres, however, a significantly improved determination of the bulk Kr abundance in Venus at the 5% level would provide fundamental insight into whether or not common sources supplied the atmospheres of all of the inner planets.

The isotopic distribution of Xe at Venus can also test the controversial “U-Xe” hypothesis invoked for Earth (Pepin, 1991). This theory maintains that the original source of Earth’s Xe, known as “U-Xe,” had an isotopic composition that was distinctively depleted in the heavy isotopes, with 8% less  $^{136}\text{Xe}/^{130}\text{Xe}$  than in the solar wind and meteorites. The Xe-isotopic distribution in Earth’s atmosphere can be fit by the sum of mass-fractionated U-Xe with a small addition of heavy isotopes from  $^{244}\text{Pu}$  decay. Without U-Xe, Earth’s Xe-isotopic distribution has been difficult to explain. If U-Xe is in fact an accurate description of Earth’s primordial Xe, then it must have come from a source that was isotopically distinct from the solar nebula as a whole. Venus also then likely accreted its Xe from this same source. Indeed, according to the U-Xe hypothesis, Venus’ atmosphere is the most likely place in the solar system to find U-Xe. If such a discovery were to be made there, the implications for Earth and Xe-isotopic heterogeneity in the inner solar system would be major.

To resolve these various scenarios of the history of the inner solar system, relatively precise Xe-isotopic ratio measurements of at least 5% accuracy are needed, sufficient to resolve well the ~20% fractionation displayed by terrestrial and martian Xe. Somewhat higher precision — ~3% — is required to measure (1) the difference in  $^{136}\text{Xe}/^{130}\text{Xe}$  between Xe derived from hypothetical U-Xe and solar wind Xe (8%), or (2) the abundance of radiogenic  $^{129}\text{Xe}$  (7%

on Earth). Fissionogenic Xe is perhaps more difficult, as its reported detection in Earth’s atmosphere, at the 4% level, is model-dependent (Pepin, 2000). However, up to 10% of the  $^{136}\text{Xe}$  on Venus could be fissionogenic, so that a ~3% measurement accuracy in the  $^{136}\text{Xe}/^{130}\text{Xe}$  ratio would likely be sufficient to determine the relative contributions of Xe sources.

### 4.3. Neon and Oxygen Isotopic Ratios: A Common Heritage for the Terrestrial Planets?

Neon in Earth’s atmosphere has an isotopic composition that is mass-fractionated with respect to that in the mantle, with a larger proportion of heavier Ne isotopes borne in the atmosphere. This suggests that isotopically-light terrestrial Ne as well as bulk Ne has escaped into space. The ~100-times-smaller bulk Ne/Ar ratio seen on Earth and Mars today (Zahnle, 1993), compared with parent nebular values (e.g., compare the Ne/Ar values for Earth and Mars against the solar values in Fig. 4), provides further evidence of Ne escape. Models of both fractionated and bulk Ne developed by Sasaki and Nakazawa (1988) demonstrate this behavior, showing that in principle, Earth could generate the observed fractionation while also depleting the bulk Ne from an originally solar nebula composition. However, Ballentine *et al.* (2005) showed that Ne-isotope abundances in magmatic  $\text{CO}_2$  well gases strongly point to the subduction of volatiles implanted in late-accreting material as the original source of Earth’s Ne and He.

Neon has three stable isotopes, providing a means by which to test whether (1) Ne on the inner planets is related by mass fractionation of a common ancient Ne reservoir located in the same region of the parent nebula, or (2) Venus, Earth, and Mars accreted Ne from different sources. Specifically, if the ( $^{22}\text{Ne}/^{20}\text{Ne}$ ,  $^{21}\text{Ne}/^{20}\text{Ne}$ ) ratios for two planets fall on the same mass fractionation line, it would imply that they shared the same source of Ne (and perhaps other noble gases and volatiles), and then evolved to their present-day ratios via escape processes. If, instead, the observed ratios do not both fall on this line, then the two planets likely began with distinct isotopic compositions originating from different source reservoirs, thus indicating that the inner planets were built from different realms of the parent nebula.

The three isotopes of O can be used in a similar manner to distinguish differences in original compositions among solar system objects (Clayton, 1993; Yurimoto *et al.*, 2006). For example, Earth and the Moon share the same distinctive O-isotope composition, which is clearly inconsistent with the make-up of nearly all meteorites, including Vesta and martian meteorites (e.g., Stevenson, 2005). Specifically, for Vesta meteorites, the  $^{17}\text{O}/^{16}\text{O}$  ratio lies about 0.02% below the Earth-Moon mass-dependent fractionation line, while the martian value lies 0.04% above it. That Earth and the Moon share nearly the same O-isotope ratio as well as the isotopic ratios of many refractory elements (Cuk and Stewart, 2012) has been somewhat puzzling, since detailed

simulations suggest that the Moon formed almost wholly from the mantle of the Earth-striking Mars-sized object (Canup, 2004). As discussed in section 2.2, however, more recent simulations (Canup, 2012) seem to indicate that the oblique impact of an Earth-sized planetesimal would have homogenized the protolunar accretion disk and Earth's mantle. We would thus expect that terrestrial mantle and lunar O, Cr, and Ti isotopes would be similar. Further isotopic comparisons will no doubt refine or refute this interesting twist on the Moon's formation.

For Venus, if it is found that its O isotopes are distinct from Earth and the Moon, then Venus accreted from a different pool of planetesimals than Earth and the Moon. If the O-isotopic ratios for Venus are similar to those found on the Earth/Moon system, it would not only show that Venus accreted from the same reservoir of materials as Earth and the Moon, but it would also suggest that the equivalence of Earth and the Moon is not so mysterious. For example, this result could suggest that the Moon may have formed from nebular materials located inside Earth's orbit.

Currently, measurements are needed for all three isotopes of Ne and O on Venus (e.g., Pepin, 2006; Zahnle, 1993). For Ne, isotopic ratios to within 5% are needed to discriminate between early evolution models. For O, an accuracy of 0.02% for the  $^{17}\text{O}/^{16}\text{O}$  ratio is required.

#### 4.4. Argon and Neon: Potential Evidence of Large Impacts

In contrast to the dearth of Xe measurements and order-of-magnitude variation in Kr results reported between the Pioneer Venus and Venera probes (Donahue and Russell, 1997) (cf. Fig. 4), reasonably precise abundances have been determined for the values of primordial (nonradiogenic) Ne and Ar. As depicted in Fig. 4, the Pioneer Venus probes showed unexpectedly high abundances of Ne and primordial Ar ( $^{36}\text{Ar}$  and  $^{38}\text{Ar}$ , some 80 times that found on Earth), indicative of an unusual source of Ne and Ar not seen in the other inner planets (Kaula, 1999).

There are three leading theories for the high abundances of Ne and Ar on Venus, two of which involve an anomalous large impact event unique to the planet. As illustrated in Fig. 6a, the first hypothesis holds that the solar wind implanted noble gases into meter-sized particles in Venus' neighborhood that later assembled into a large, several-hundred-kilometer-scale planetesimal that eventually struck the planet (McElroy and Prather, 1981; Wetherill, 1981). Thus the Sun is the source of enhanced Ne and Ar, delivered via a very large, "solar-contaminated" impactor. Sasaki (1991) showed that this model can work in the more realistic context of an optically thick, vertically extended dust disk generated by collisions between planetesimals.

A second theory maintains that a large comet from the outer solar system delivered Ar and Ne trapped in cold cometary ices (Owen et al., 1992). The impactor would need to have been  $\geq 200$  km in diameter to supply the large Ar content found in Venus, assuming the bolide had the

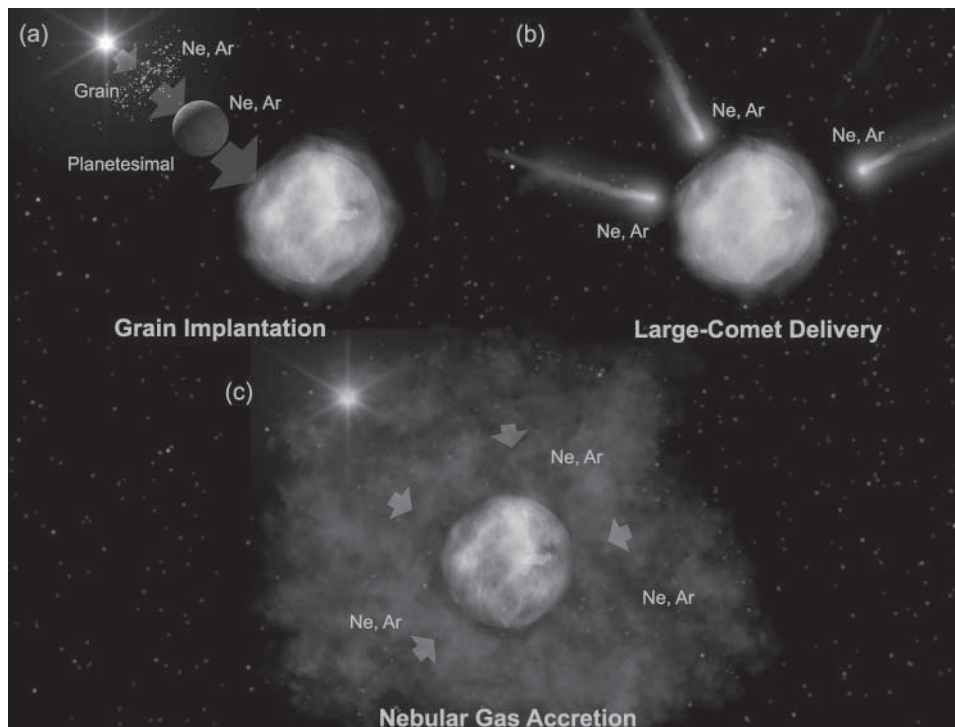
same Ar-rich make-up as that of the hypothetical polluters of Jupiter's atmosphere (Zahnle, 1993). More recently, Gomes et al. (2005) estimate that  $\sim 10^{23}$  g of cometary material was delivered to Venus and Earth during the late heavy bombardment, corresponding to the mass of a dozen 200-km-diameter comets (cf. Fig. 6b). Thus, if such cold comets existed — as suggested by the enhanced noble-gas abundances on Jupiter measured by the Galileo probe (Mahaffy et al., 2000) — the Gomes et al. (2005) result implies that there is little difficulty in such objects delivering enough Ar from the outer solar system.

A third theory holds that the terrestrial planets gravitationally captured Ar and Ne directly from the local solar nebula (Fig. 6c). Due to its thicker, more protective atmosphere, Venus was significantly better than Earth and Mars at preserving its atmosphere against giant impacts (Genda and Abe, 2005).

These theories can be distinguished via precise (1–3%) *in situ* measurement of  $^{36}\text{Ar}/^{38}\text{Ar}$  in Venus' atmosphere as well as the telltale Xe-isotopic ratios noted earlier. In particular, such sampling can reveal whether the solar wind ratio, currently under analysis by the Genesis mission (e.g., Grimberg et al., 2007), is found on Venus. Prior Pioneer Venus probes measured the  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio on Venus to an accuracy of only 10% (Oyama et al., 1980), too crude to determine if the planet's signature is that of the solar wind, based on early Genesis results.

#### 4.5. Radiogenic Argon and Helium: A Record of Planetary Degassing

Radiogenic Ar and radiogenic and nonradiogenic He are powerful probes of mantle degassing. Created underground by the decay of K,  $^{40}\text{K}$  (half-life of 1.3 G.y.), radiogenic  $^{40}\text{Ar}$  diffuses upward through the mantle and is emitted into the atmosphere. Compared to Earth's atmosphere, Venus has about 25% as much atmospheric radiogenic  $^{40}\text{Ar}$ . This strongly implies that, compared to Earth, either (1) Venus has markedly less K, or (2) the planet has degassed less (Turcotte and Schubert, 1988). A plausible scenario for (2) would be a large decrease in Venus' rate of degassing approximately 1 b.y. after formation. The low  $^{40}\text{Ar}$  abundance coupled with the very high  $^{36}\text{Ar}$  content results in a  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio near unity, significantly less than the range of  $\sim 150$ –2000 measured for Earth, Mars, and Titan (Owen, 1992; Atreya et al., 2006, 2007) indicative of active geologies. However, recent laboratory studies on the compatibility of Ar in silicate melt indicates that  $^{40}\text{Ar}$  may not be indicative of interior degassing efficiency (Watson et al., 2007). Instead, the abundance of  $^{40}\text{Ar}$  in Earth's atmosphere may be due largely to the hydrological weathering of the crust. If this is the case, the amount of  $^{40}\text{Ar}$  seen in Venus' atmosphere may indicate that it has experienced about one-fourth of the aqueous weathering that Earth has over the age of the solar system. Further laboratory work on the compatibility and diffusion of Ar in the mantle is needed to understand exactly what processes are responsible



**Fig. 6.** See Plate 4 for color version. Schematics of the three main hypotheses for the origin of large Ne and Ar abundances in Venus' atmosphere. **(a)** Grain implantation. Early solar wind fluxes were many orders of magnitude higher than today. Solar-wind Ar and Ne implanted into grains around the Sun, which coalesced into Ar,Ne-rich planetesimals that impacted Venus. **(b)** Large-comet delivery. Argon and Ne frozen and trapped in cometary ice lattices was delivered by one or more large comets ( $\geq 200$  km diameter) from the cold reaches of the outer solar system, leaving Venus with an Ar,Ne-rich atmosphere. **(c)** Nebular gas. Venus' present atmosphere came directly from the nebula in which it was formed. The atmosphere survived relatively intact against subsequent impactors that blew off the original atmospheres of Earth and Mars, resulting in a relatively Ar,Ne-rich atmosphere on Venus.

for the  $^{40}\text{Ar}$  abundance in terrestrial planetary atmospheres.

Helium provides another probe of planetary degassing through time. There are two stable He isotopes: the abundant  $^4\text{He}$  and the much rarer  $^3\text{He}$ . On Earth, more than 90% of the  $^4\text{He}$  is radiogenic, primarily created by the decay of U and Th (with relevant half-lives of 0.7, 4.5, and 12 b.y.), while most of the terrestrial  $^3\text{He}$  is primordial. Earth's continents are granitic and are strongly enriched in Th and U, and thus they are a major source of  $^4\text{He}$ . The mantle is a source of both isotopes, with a ratio of 90,000:1 (Jambon, 1994). Degassing of primordial  $^3\text{He}$  indicates that Earth's interior still retains a noble-gas imprint that dates to its formation. For Mars, EUV observations of the 584-Å He line indicate that the He mixing ratio in the lower atmosphere is  $4 \pm 2$  ppm (Krasnopolsky and Gladstone, 1996). Coupled with models of the production and outgassing of  $^4\text{He}$  and its escape to space, these authors conclude that He outgassing rate on Mars is 2–4 times smaller than its escape. Similarly, measurements of  $^3\text{He}$  and  $^4\text{He}$  on Venus should provide insights into the degree of mantle degassing and

associated active geology on Earth's sister world (Namiki and Solomon, 1998).

While He escapes quickly from Earth's atmosphere, loss rates are significantly slower from Venus (Donahue and Russell, 1997). If there really has been very little atmospheric escape over the eons on Venus, then about twice as much radiogenic  $^4\text{He}$  would be expected as radiogenic  $^{40}\text{Ar}$  (assuming an Earth-like K/U ratio). Yet less  $^4\text{He}$  is observed. If  $^4\text{He}$  escaped, then the corresponding  $^3\text{He}$  escape rate should be greater, thereby reducing the  $^3\text{He}/^4\text{He}$  ratio. Alternatively, a high  $^3\text{He}/^4\text{He}$  ratio in the current atmosphere implies either (1) a relatively small He escape rate, (2) a relatively recent and large mantle degassing event that released primordial  $^3\text{He}$ , or (3) a dearth of near-surface  $^4\text{He}$ -producing granitic material (Turcotte and Schubert, 1988). New insights into the geology, outgassing history, and evolution of Venus would be provided by better information on both the isotopic ratios and escape rates of He, the former to a measurement accuracy of approximately 20%. The He escape rates are currently under investiga-



tion by the Venus Express Analyser of Space Plasma and Energetic Atoms (ASPERA) experiment (e.g., Galli et al., 2008). What remains, then, is more accurate atmospheric measurements of the He-isotopic abundances.

## 5. ISOTOPES OF LIGHT GASES: ATMOSPHERIC LOSS THROUGH TIME

### 5.1. Isotopes of Hydrogen and Nitrogen: Possible Loss of an Ancient Ocean

Primarily due to (1) the lack of a protective internally-generated magnetic field and (2) a strong greenhouse effect, the atmosphere of Venus today is vastly different from that at the end of its formation period some 3.8 G.y. ago. Perhaps the single most significant change on Venus was the loss of the bulk of its water over the eons, as evidenced by the large ratio of deuterated (heavy) water (HDO), relative to H<sub>2</sub>O, observed today that indicates that the D/H ratio is some 150 times that found on Venus' sister planet, Earth (Donahue, 1999). Potential mechanisms responsible for this high D/H ratio range from the rapid loss of a primordial ocean into space to steady-state mechanisms promoting the idea that atmospheric water is supplied by volcanic outgassing and cometary infall (Grinspoon, 1993). The D/H of Earth's water is similar to the chondritic value, suggesting that chondritic bodies were the main source of Earth's volatiles (Alexander et al., 2012). However, if Venus' primordial water came from comets, the D/H of the source may have been higher than Earth's present value. Most comets exhibit a D/H of about twice that found on Earth (Mousis et al., 2000), although Hartogh et al. (2011) reported a Jupiter-family comet with an Earth-like chondritic D/H. When water in Venus' atmosphere was photodissociated, the O was lost via the oxidation of Fe-bearing crustal minerals and H escape out of the atmosphere. The escape of H is facilitated by the absence of a magnetic field that then allows the solar wind to energize and drag away H atoms from the top of the atmosphere.

A fundamental question is the abundance of water at the end of the planet's formation period, estimated to be equivalent to a global ocean between 5 and 500 m in depth (Donahue et al., 1997). The large uncertainty arises from several factors, including imprecise estimates of the global mean D/H ratio, which the Venus Express mission found to vary significantly with altitude (Federova et al., 2008), possibly due to photochemical fractionation effects (Liang and Yung, 2009). Another source of uncertainty is the fractionation factor for the escape of H and D and how this factor has varied with time, as differing loss processes have dominated. Over the full range of measurement uncertainties, the D/H ratio ranges from 0.013 to 0.038, based on data from the Pioneer Venus probe mass spectrometer and infrared spectrometer (Donahue, 1999) and the Ultraviolet and Infrared Atmospheric Spectrometer (SPICAV/SOIR) onboard Venus Express (Bertaux et al., 2007; Federova et al., 2008). If escape fluxes are in the upper end of the range

suggested by pre-Venus Express data,  $>3 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ , then the greatly enhanced (over terrestrial) D/H ratio must reflect loss over the last 0.5 G.y., masking a primordial signature (Grinspoon, 1993; Donahue, 1999). The escape flux and ocean volume is presumably even greater for the most recent Venus Express D/H ratio of  $240 \pm 25$  times the Earth ocean value reported by Federova et al. (2008) for Venus' upper atmosphere. Also, if a large amount of H and D loss occurred during an early phase of fractionating hydrodynamic escape, driven by an intense early solar EUV flux (Chassefière, 1996), then the original water inventory could have been many times larger than the values indicated by the D/H ratio seen today.

Additional information on Venus' atmospheric loss comes from the isotopic ratio of N, <sup>15</sup>N/<sup>14</sup>N. Currently the venusian ratio ( $3.8 \pm 0.8 \times 10^{-3}$ ) is known to  $\pm 20\%$ , comparable to the terrestrial value ( $3.7 \times 10^{-3}$ ) and broadly similar to N in meteorites (Donahue and Pollack, 1983), but at variance with the atmospheres of Mars ( $5.9 \pm 0.5 \times 10^{-3}$ ) and Jupiter ( $2.2 \pm 0.3 \times 10^{-3}$ ) (Owen et al., 1977; Owen, 1992; Abbas et al., 2004). The consensus scenario is that Earth and Mars accreted their N from a common meteoritic or chondritic source. However, on low-gravity Mars, the light N preferentially escaped, resulting in a relatively high <sup>15</sup>N/<sup>14</sup>N ratio. In contrast, the low <sup>15</sup>N/<sup>14</sup>N ratio on Jupiter pertaining to a relatively high light N component means that Jupiter's N was supplied by a cometary or nebular source (Owen and Bar-Nun, 1995). Since Venus and Earth have approximately the same <sup>15</sup>N/<sup>14</sup>N ratio, the expectation is that Venus also accreted its N from the same common source as Earth and Mars. Comparison of the N isotopes between Venus and Earth should help determine whether N escape was significant on at least one of the two planets. In summary, *in situ* measurements of the isotopic ratios of <sup>15</sup>N/<sup>14</sup>N and HDO/H<sub>2</sub>O to 5% — the latter over a range of altitudes to assess photochemical and escape fractionation effects — would provide insights into understanding (1) present and past escape rates, (2) the nature of Venus' likely water-rich ancient climate, and (3) the role of comets in supplying volatiles to the inner planets.

### 5.2. Sulfur Isotopes: Probes of Current Degassing

The isotopic ratios of S, <sup>33</sup>S/<sup>32</sup>S and <sup>34</sup>S/<sup>32</sup>S, are established in volcanic and interior processes. Measurements of these ratios in the venusian atmosphere therefore potentially provide information on interior degassing during recent geologic times. However, S-isotopic ratios are susceptible to modifications via (1) photochemical fractionation processes involved in the atmospheric S cycle and (2) surface chemistry involving Fe sulfides. Indeed, anomalous fractionations — deviations from simple mass-dependent fractionation — as large as 7% have been measured in laboratory experiments at 193 nm (Farquhar et al., 2004). Yet in practice, natural samples that have not been biologically fractionated show anomalous fractionations of a few tenths of a percent at most and conventional fractionations

less than 1%. For Mars, the largest anomalous fractionation measured in an escaped meteorite is 0.1% (Farquhar *et al.*, 2007). Precise S-isotopic measurements at the surface of Mars at the 0.1% level will be obtained shortly by the Mars Science Laboratory (Mahaffy *et al.*, 2012).

For Venus, useful measurements of the  $^{34}\text{S}/^{32}\text{S}$ - and  $^{33}\text{S}/^{32}\text{S}$ -isotopic ratios begin at the 1% level, sufficient to provide quantitative constraints on anomalous isotopic effects in photochemical hot spots. To discriminate reaction pathways, 0.1% precision is needed. Due to the atmospheric photochemical fractionation process, accurate characterization of S isotopes requires multiple samples obtained in a variety of thermochemical environments, during both day and night and over a variety of altitudes.

Water and its isotopologue HDO are also potential tracers of volcanic activity. Measurements of the abundances of magmatic  $\text{H}_2\text{O}$  and HDO released in a venusian volcanic eruption would provide unique information distinguishing recent volcanic sources from primordial or exogenic sources. This would provide insights into (1) the current rate and history of volcanic activity, (2) the efficacy of present theories of global tectonics, (3) constraints on the oxidation rate of the crust, and (4) the overall evolution of the current  $\text{H}_2\text{O}$ -poor atmosphere.

## 6. CONCLUSIONS

An alien visitor to our young solar system 4.1 b.y. ago would have likely found a very intriguing trio of planets situated between 0.7 and 1.7 AU from the Sun. Only ~450 m.y. old at that time, each would probably have been enshrouded by a substantial greenhouse atmosphere overlaying a surface adorned with seas of liquid water. After 300 m.y. of relative tranquility following the end of planetary accretion, our visitor would likely find primitive one-celled life flourishing on at least the middle planet, Earth. But conditions on the others would seem conducive to life as well, with atmospheres composed — as on Earth — mostly of  $\text{CO}_2$ , Ni, and water. The alien explorer would note that Earth has two major physical differences that set it apart from the others: First, it is enshrouded by a significant magnetic field that protects it from the Sun's onslaught of charged particles, and second, it is attended by a large satellite orbiting just 25,000 km away (Ida *et al.*, 1997) that keeps the planet's spin axis remarkably stable. Given these differences, the wondering visitor may have contemplated what would evolve on these planets during the ensuing eons. Our investigator may have wondered whether, given other potentially important conditions — such as the solar flux of both light and charged-particle radiation, the rotation rate and inclination of planetary spin, and the possibility of occasional bombardment by the remaining detritus of asteroids and comets — their atmospheres, hydrospheres, and geologies would all significantly change over the eons. And if they did, would they evolve in a similar or disparate manner? That intriguing story is the subject of the remainder of this book.

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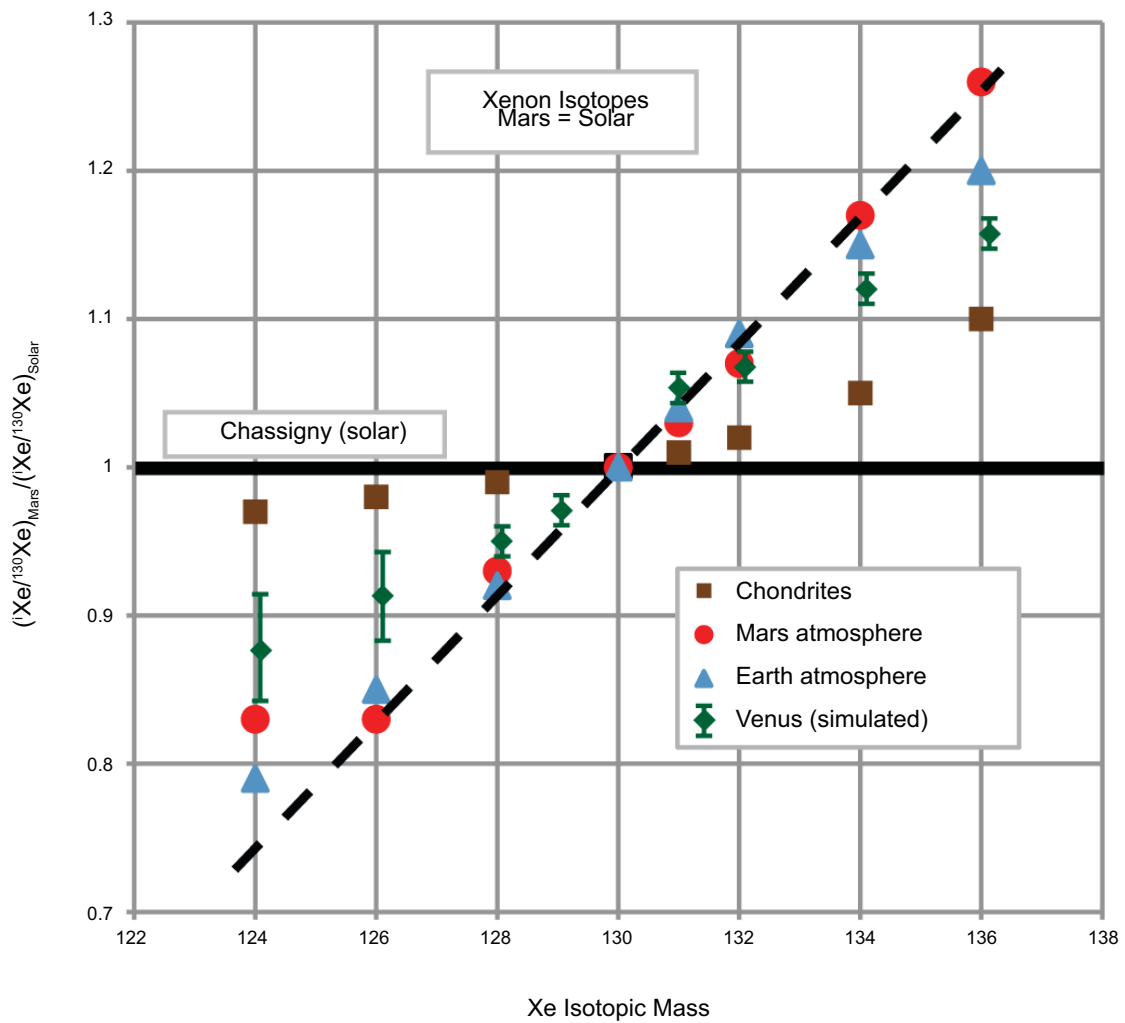
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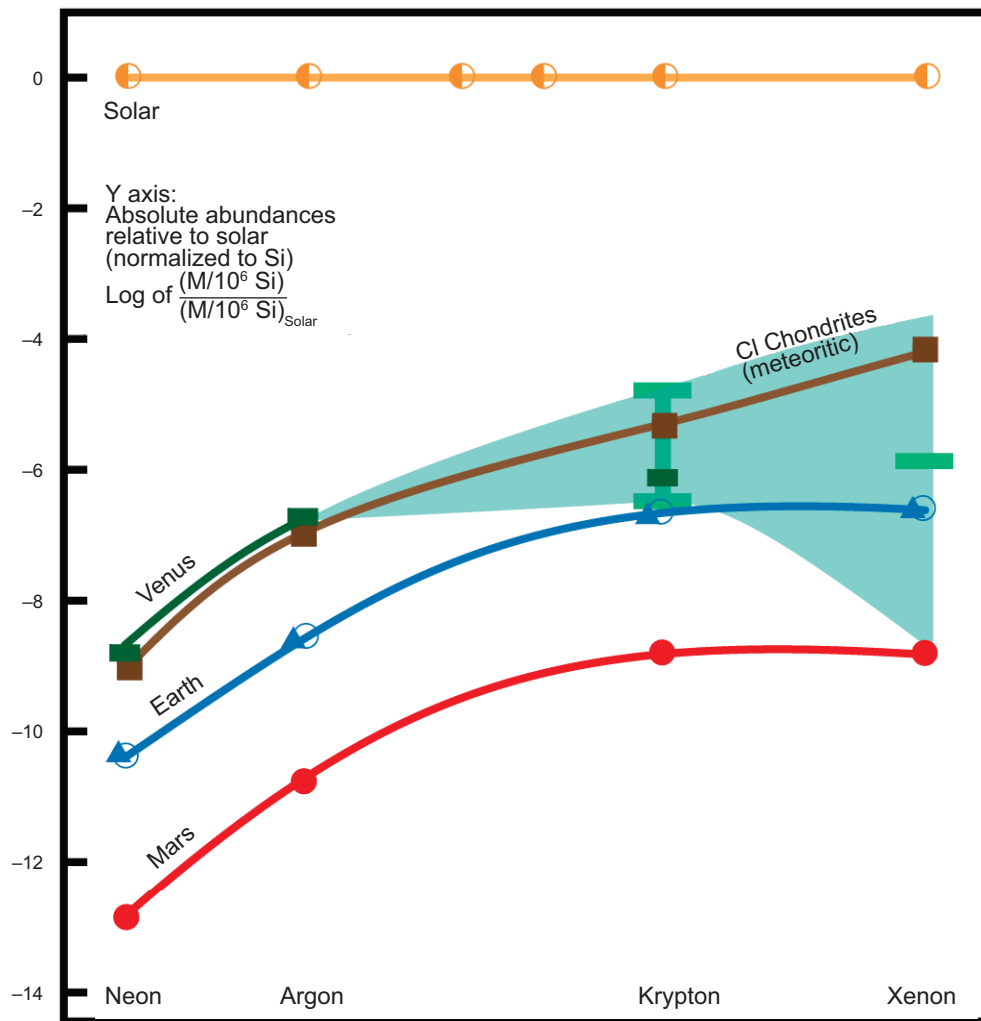
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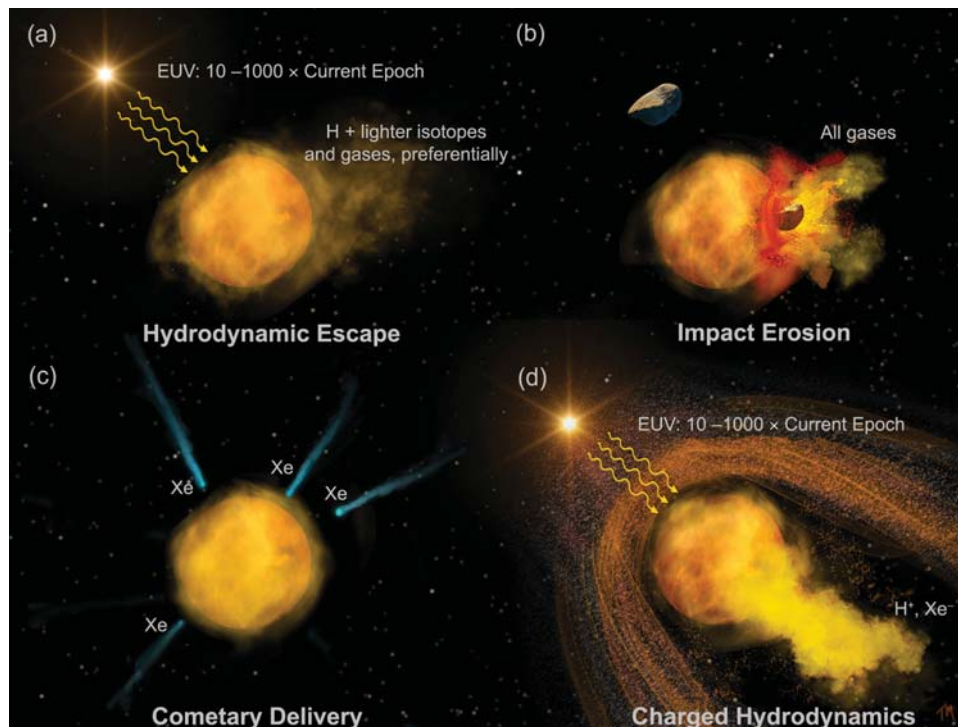
**Plate 1.** Fractionation of Xe isotopes. Possible Venus Xe fractionation pattern observed by a future *in situ* mission is depicted (green) compared to the patterns of Earth, Mars, chondrites, and the Sun (after *Bogard et al., 2001*). A common Venus/Earth/Mars pattern would bolster the hypothesis that a common source of comets or large planetesimals delivered volatiles throughout the inner solar system. A different pattern for Venus would strengthen the solar EUV blowoff theory.

Accompanies chapter by Baines et al. (pp. xx–xx).



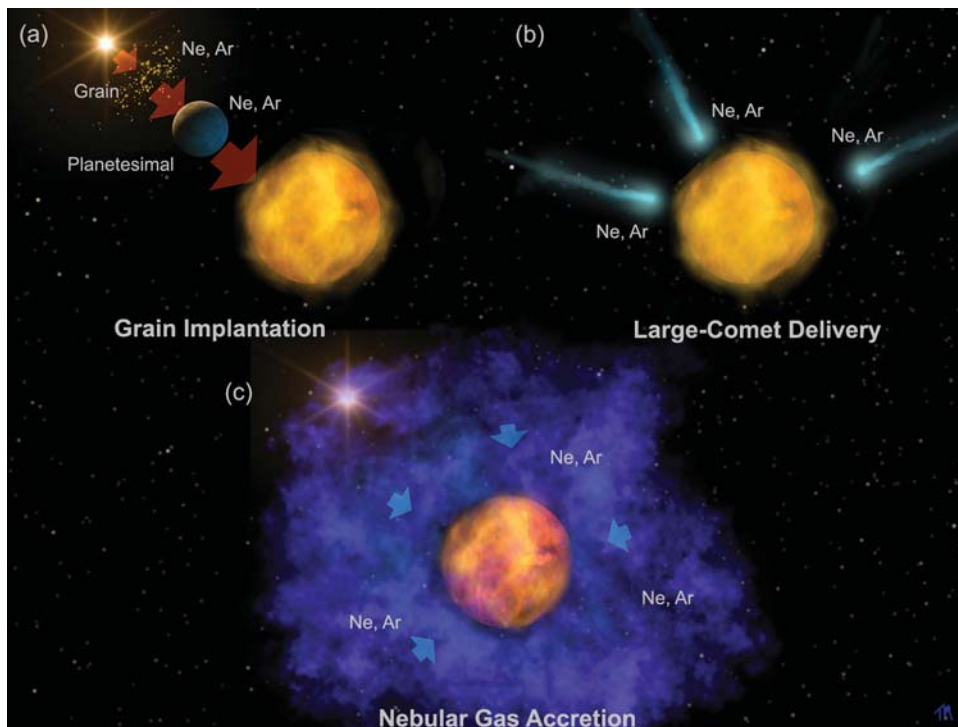
**Plate 2.** Noble gas abundances for Earth, Mars, Venus, chondrites, and the Sun (after *Pepin, 1991*). Missing Xe and poorly constrained Kr data for Venus are critical for understanding the history of its early atmosphere. For Ne and Ar, and likely Kr, Venus is more enhanced in noble gases vs. Earth and Mars, likely indicating (1) a large blowoff of the original atmospheres of Mars and Earth, and/or (2) enhanced delivery of noble elements to Venus from comets and/or solar-wind-implanted planetesimals. For Venus, the unknown/poorly constrained Xe/Kr and Kr/Ar ratios — denoted by the range of slopes of the aqua area — are consistent with all solar system objects shown, including (1) a solar-type (Jupiter and cometary) composition (orange line), (2) a chondritic composition (brown line), and (3) the composition of Earth and Mars (blue and red lines).

Accompanies chapter by Baines et al. (pp. xx–xx).



**Plate 3.** Schematics showing major features of the four main hypotheses of early planetary evolution that led to atmospheric Xe-isotopic abundances on the terrestrial planets. **(a)** Hydrodynamic escape. Early solar EUV was 100–1000 times more intense than today, heating the atmosphere to the point where H began to flow out of the exosphere. It dragged lighter molecules with it, fractionating the atmosphere so that it was isotopically heavier. **(b)** Impact erosion. Small impacts both added material and eroded the atmosphere. Large impacts blew off most of the atmosphere above the plane of impact, indiscriminate of mass, so no fractionation occurred. **(c)** Cometary delivery. Cold comets from the outer solar system with trapped Xe incorporating the isotopic ratios of the cold outer solar system impacted the surface. **(d)** Charged hydrodynamics. Hydrogen and Xe are both easily ionized, unlike other molecules. Thus ionization by the UV or solar wind preferentially allowed H and Xe to escape, while also allowing somewhat smaller portions of other ionized atoms and molecules to go along for the ride. The process is fractionating, dependent upon both mass and ionization energy.

Accompanies chapter by Baines et al. (pp. xx–xx).



**Plate 4.** Schematics of the three main hypotheses for the origin of large Ne and Ar abundances in Venus's atmosphere. **(a)** Grain implantation. Early solar wind fluxes were many orders of magnitude higher than today. Solar-wind Ar and Ne implanted into grains around the Sun, which coalesced into Ar,Ne-rich planetesimals that impacted Venus. **(b)** Large-comet delivery. Argon and Ne frozen and trapped in cometary ice lattices was delivered by one or more large comets ( $\geq 200$  km diameter) from the cold reaches of the outer solar system, leaving Venus with an Ar,Ne-rich atmosphere. **(c)** Nebular gas. Venus' present atmosphere came directly from the nebula in which it was formed. The atmosphere survived relatively intact against subsequent impactors that blew off the original atmospheres of Earth and Mars, resulting in a relatively Ar,Ne-rich atmosphere on Venus.

Accompanies chapter by Baines et al. (pp. xx–xx).