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Atmospheres on the terrestrial planets: Clues to origin and evolution

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Abstract

Earth, Venus and Mars reached their final sizes in the first 100 Myr or so of solar system history. For part of that time the growing planets and the materials forming them were immersed in the Sun-like gases of the solar nebula, and so one would expect that their early volatile inventories were acquired from the nebula. But the compositions of atmospheres presently on these planets are *not* solar, and therein lies a complex and fascinating story of physical and chemical evolution over the past 4.5 Ga. Records of physical processing survive most clearly in the chemically inert noble gases, and data on the elemental and isotopic abundances of these trace constituents, now from Mars and Venus as well as Earth, point to atmospheric histories punctuated by enormous inputs of energy from early astrophysical sources long since vanished. Observational and theoretical advances during the past 30 years underpin current evolutionary models in which primordial solar-like atmospheric gases are fractionated by gravitational escape, driven on Earth by a giant Moon-forming impact, on Mars by sputtering at high altitudes, and on all three planets by adsorption of intense ultraviolet radiation from the young Sun. Residual atmospheres left behind after these outflows to space are augmented by planetary degassing, including species generated in their interiors by radioactive decay. Interplay over time of these mechanisms for loss and gain of atmospheric gases can account for many of the details of contemporary noble gas distributions. These of course are just models. However they have predictive power for compositions as yet unmeasured, particularly on Venus, and the modeling assumptions are in principle testable by experiment or theory. The fundamental question of whether nature actually shaped the atmospheres in this way is still unanswered, but at least we have an outline of how it might have happened.

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1. Atmospheres on (and in) the terrestrial planets: Why are they interesting?

What is an atmosphere? For this discussion we define it as a gravitationally bound reservoir of species volatile enough at local temperatures to exist as gases above a

planetary surface, and dense enough that its physics is dominated by collisional interactions. Among bodies sunward of the asteroid belt, this includes Mars, Earth and Venus but not Mercury or the Moon. Space above these latter bodies is not empty, but its thin populations of atoms, released by outgassing or surface heating, describe ballistic orbits that terminate either in escape or re-impacts with the surface. These “collisionless” atmospheres are episodic and transient, and do not preserve the integrated clues to evolutionary history present in more permanent atmospheric reservoirs.

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The three qualifying atmospheres are strikingly different. Pressures decline outward from Venus to Earth by two orders of magnitude, and by a similar factor from Earth to Mars. Carbon dioxide is the principal species on Mars and Venus; on Earth, it's nitrogen. One can rationalize Mars' skimpy atmosphere; with a mass ten times smaller than Earth's, Mars may never have accumulated a comparable inventory of volatiles, and these would have been more susceptible to escape from the planet's relatively weak gravity over time. Differences in atmospheric pressure and composition between Earth and Venus seem harder to understand. One might expect that these "sister" planets, not very different in mass or distance from the sun, would have acquired similar "primordial" atmospheres in their youth and followed similar evolutionary paths to the present. In fact, their principal volatile inventories today actually are comparable *if* we include the carbon dioxide locked up as carbonates in Earth's sedimentary column. Released to the atmosphere, this sequestered CO₂ would transform Earth into an instant Venus with about the same surface pressure. Earth apparently was spared this fate by the early presence of liquid water which took up atmospheric CO₂ and precipitated it as carbonate rock. This contrasting evolution must have hinged critically on temperature conditions, governed in part by differing heliocentric distance, which allowed water to exist on Earth's surface but not on Venus.

Understanding how primordial atmospheres evolved to their present compositions is closely connected to the challenge of understanding the evolution of the planets themselves, in particular their geophysical histories of differentiation and outgassing, and emergences of coupled atmosphere-interior systems. And interest in volatiles extends beyond their relationship to a single planet's initial state and the mechanisms that drove it down its specific evolutionary track. Attempts to decipher volatile histories in the broader context of evolution of the solar system as a whole are focusing attention on the sources and processing of gases in the solar accretion disk, comets, primitive meteorites, and planets as a class.

We have no model-independent ways to assess the relative importance of possible primordial sources and evolutionary processes in shaping present-day atmospheres. Much of the following discussion is therefore about models, and their assumptions about the origins, compositions, and lifetimes of primary reservoirs, the mechanisms responsible for transporting and fractionating volatiles, and the environments in which such processes operated. The objective is to account in detail for contemporary elemental and isotopic compositions. There's been much progress toward this end since

serious study of the subject began in the 1940s with pioneering papers by Brown [1] and Suess [2]. But we are not there yet.

2. Tracers of atmospheric origin and evolution

Efforts to unravel atmospheric histories have focused on the noble gases as evolutionary tracers. Free from the entanglements of chemical interactions, compositions of these minor constituents are clues to the characteristics of their source reservoirs, and are ideal recorders of mass fractionations imprinted by physical processing such as escape from planetary gravitational fields. Nitrogen, chemically inert in molecular form, is another potentially useful tracer.

3. In the beginning: Primordial atmospheres

As they grew to their final masses, first by accretion of small bodies ("planetesimals") into Moon-to-Mercury size "planetary embryos" in 0.1 to 1 million years (Myr), then by merger of these embryos over the next ~100 Myr [3,4], the terrestrial planets had several opportunities to acquire primary atmospheres. Gravitational capture from the surrounding accretion disk – the solar nebula – is one possibility. Another is volatiles carried into the growing planets by infalling planetesimals and dust; here contributions could include gases similar to those found in primitive meteorites, and gases in dust grains, either adsorbed from the nebula [5] or implanted by the solar wind [6]. Comets scattered inward from the outer solar system would have carried noble gases as well as water, carbon, and nitrogen into inner planet accretion zones [7]. Noble gas distributions in comets are still unknown, but solar isotopic compositions, perhaps somewhat modified by trapping fractionations [8], are expected in ancient icy matter that trapped volatiles from the outer nebula.

An attractive source for Earth and Venus is direct capture from the nebula. Gravitational condensation of primordial atmospheres requires planetary growth to appreciable fractions of their present masses before the nebula gas phase dissipated. Observational and theoretical estimates of nebular lifetime are ~10 Myr [9]; ~60% of Earth's mass is thought to accumulate in ~10–20 Myr [3,10]. So the nebula could have survived long enough for the planets to capture substantial atmospheres. Atmospheric gases overlying planetary surfaces melted by accretional energy and the thermal blanketing effect of the atmospheres may also have populated internal reservoirs by dissolution and downward mixing, loading parts of the interiors with

isotopically solar noble gases [11,12] and nitrogen [13] that later degassed. More inefficient capture by sub-planetary bodies is also possible. Protoplanetary cores growing to a few lunar masses in the nebula can condense tenuous atmospheres [14]. Atmospheric gases adsorbed on these planetary embryo surfaces might survive as deeply-seated volatile reservoirs in the fully assembled planets.

There is no consensus on whether Mars is massive enough to have condensed appreciable abundances of ambient gases. Modeling estimates of primary atmospheric pressures on a Mars-mass planet range from small [14–16] to substantial ([17], Table 1). In the first case, regardless of the plausibility of gravitational capture as the source of primary atmospheres on Venus and Earth, some other way would be needed to supply Mars.

What were the compositions of nebular noble gases, long since dissipated to space? Two proxies survive: the solar wind, reflecting the Sun’s isotopic composition within relatively small transport fractionations [18,19], and the captured atmospheres of the giant planets — especially Jupiter’s, for which there are now measurements by the Galileo Probe [20]. We will see later that the solar wind data in particular are central in evolutionary modeling.

4. Atmospheres now

Major species compositions provide some insight to atmospheric histories. More decisive evidence is carried by the noble gases. The data are illuminating but by no means complete. Abundances and isotopic distributions are accurately known for Earth’s atmosphere, but are less well determined for Mars and imprecisely if at all for Venus. And we know comparatively little about the compositions of the second “atmospheres” on all three planets — gases trapped in their interiors. These are important because planetary outgassing in the past would have contributed to exterior atmospheres. On Earth the volatile flow is probably in both directions, upward by eruption at mid-ocean ridges, ocean islands, and gas wells, and downward by subducting oceanic crust and sediments carrying trapped surface volatiles. Characterizing the compositions and histories of volatile reservoirs within the Earth is an active and challenging area of research (e.g., [21–27]). For Mars we know little about interior gases except for xenon [28], and for Venus nothing.

Nevertheless the information in hand is rich in clues to atmospheric evolution. Elemental abundances — excluding He, which is gravitationally unbound — in the atmospheres of Earth, Venus and Mars, and in primitive meteorites, are shown in Fig. 1. Noble gases in these

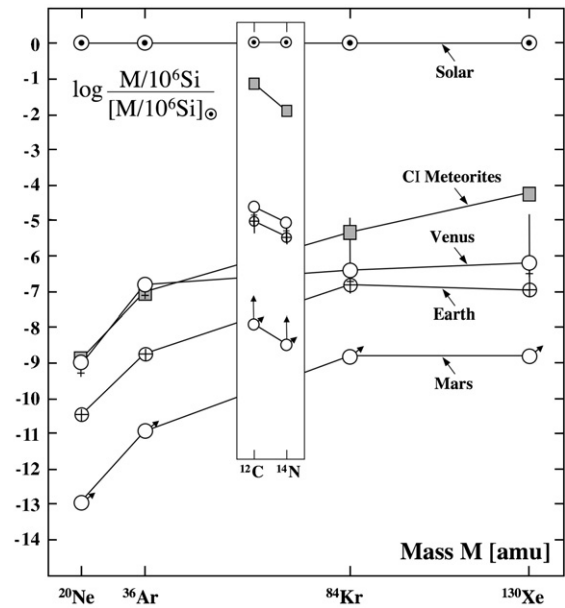


Fig. 1. Abundances of Ne, Ar, Kr, and Xe in terrestrial planet atmospheres and in primitive (CI) meteorites, represented relative to solar abundances in units of atoms per 10^6 Si atoms ([14] and references therein). These noble gas depletion patterns were probably created from initially solar compositions by different processes acting in atmospheres and meteorites, on planets by gravitational escape and outgassing as discussed in the text, and in the meteorites by mass-dependent adsorption mechanisms [5]. Carbon and nitrogen abundances are shown in the inset. For Earth they include estimates of C and N trapped in crustal reservoirs as well as atmospheric inventories. Calculated in this way, abundances of both species are nearly identical on Earth and Venus, as noted in Sec. 1.

reservoirs display large and planet-specific depletions with respect to solar abundances; their isotopic patterns are generally distinct from each other and from inferred solar compositions. Information for Venus comes from atmospheric measurements by mass spectrometers on the Venera and Pioneer Venus spacecraft [18,29]. The data, while partial and uncertain, are nonetheless impressive for instruments operating in extreme environmental conditions. Mars is more hospitable to spacecraft, but even there the data returned by spectrometers on the Viking landers [30,31] are generally not precise enough to adequately constrain models of atmospheric history. However the entire field of Martian evolutionary studies became much more quantitative with the recognition that a class of meteorites, collectively called the SNC group, almost certainly come from Mars, and, in a real stroke of luck, gases from its atmosphere were apparently trapped in shock-melted phases of these meteorites as they chilled to glass [32–39]. Fig. 2 compares elemental abundances in glass

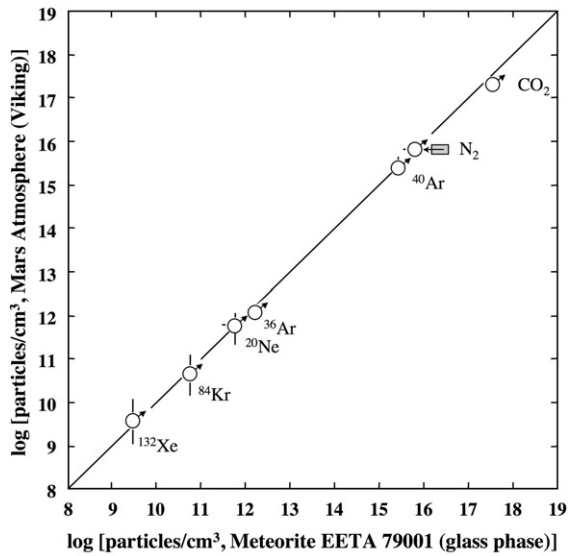


Fig. 2. Comparison of gas abundances trapped in glassy phases of the SNC meteorite EETA79001 with measurements of the Martian atmosphere by the Viking spacecraft [35,36] and references therein. The agreement extends over some nine orders of magnitude in partial pressures. Atmospheric species were apparently trapped in the shock-produced glass with efficiency close to 100%, as shown by the distribution of the data along the plot bisector. The mechanism that produced this remarkable 1:1 emplacement into the glass is not understood [36].

from a Shergottite – the “S” in “SNC” – with Viking atmospheric measurements [35,36]. The striking agreement of the two data sets is compelling evidence that the SNCs are Martian. The happy advent of these meteorites opened the window to laboratory analyses of Mars’ atmospheric gases with far higher precision than is possible for flight instruments.

Nitrogen, the adopted “noble gas”, has two isotopes. There is much debate about the origins of the wide range displayed by nitrogen isotope ratios in solar system bodies (Fig. 3). An intriguing result from Viking was measurement of a spectacular $\sim 60\%$ enrichment in ^{15}N relative to ^{14}N on Mars compared to Earth [30], attributed to preferential loss of the lighter isotope in escape processes operating over time high in the Martian atmosphere [40–42]. This composition is plotted in the lower panel of Fig. 3 along with the uncertain value for Venus. It’s clear from the rest of the figure that interpreting nitrogen isotopic distributions in the solar system is a complicated business. We will return to this later.

5. Evolution from primordial states

Many mechanisms could have contributed to gain or loss of primordial planetary gases. Some probably pre-

serve compositional signatures — i.e., they do not fractionate elements or isotopes. Among these are gravitational gas capture, solar wind implantation, impact-degassing of accreting matter, and atmospheric ejection by large bodies impacting into pre-existing atmospheres. Others primarily fractionate only elements: examples include solution [11] or adsorption [14] of atmospheric gases into growing planets. In contrast, gravitational escape of atmospheric constituents is intrinsically mass-dependent, no matter the specific loss mechanism, and so both elements and isotopes in the residual atmospheres are fractionated with respect to initial compositions.

Noble gases on Mars, Earth and Venus carry powerful evidence that their primordial parents had solar compositions, and that gravitational escape played a major role in their evolution. Planetary gases in Fig. 1 are increasingly depleted with decreasing mass, consistent with lighter species escaping more readily from gravity fields. Isotopic distributions are even more diagnostic of losses from early solar-like atmospheres. From Ne through Xe on Mars and Earth, and for Ne and Ar on Venus (where Kr and Xe compositions are unknown), *all* atmospheric isotope ratios are “isotopically heavier” than their solar counterparts — i.e., lighter isotopes are preferentially depleted relative to heavier ones. These depletions are smoothly mass-dependent fractionations of solar-wind ratios, excluding only species produced by nuclear processes in planetary interiors and degassed to atmospheres after escape had run its course.

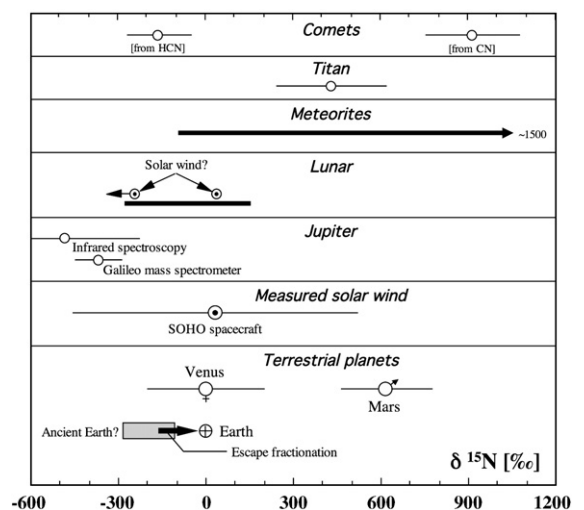


Fig. 3. Nitrogen isotope ratios in the solar system, plotted as permil (‰) deviations of measured $^{15}\text{N}/^{14}\text{N}$ from the standard, here the terrestrial air ratio: $\delta^{15}\text{N} = 1000 \{ [(^{15}\text{N}/^{14}\text{N})_{\text{measured}} / (^{15}\text{N}/^{14}\text{N})_{\text{air}}] - 1 \}$ ‰. Earth by definition plots at 0‰. See text for references.

If atmospheric noble gases are fractionated remnants of solar-like progenitors, what were the escape mechanisms, and what powered them? Losses from the outer reaches of planetary atmospheres are an old and well-studied subject [43,44]. Mechanisms operating today on the terrestrial planets cannot remove species as massive as the heavy noble gases, and yet there is clear evidence that mass-dependent loss signatures are imprinted on atmospheric Ar, Kr and Xe isotopes. This has focused attention on earlier epochs of planetary histories, when now-vanished energy sources could have driven intense outflows of atmospheric gases in a process called hydrodynamic escape or “blowoff” [14,41,44–49].

5.1. Hydrodynamic escape

Hydrodynamic escape occurs when hydrogen-rich primordial atmospheres are strongly heated, either at high altitudes by intense extreme-ultraviolet (EUV) radiation from the young sun [14] or by energy deposited in a giant impact [48]. The heated hydrogen escapes to space, and in the process its outward flow exerts upward drag forces on heavier atmospheric constituents. With powerful energy input, escape fluxes can be large enough to lift species as massive as Xe entirely out of terrestrial planet atmospheres [14,46]. Lighter species are more readily entrained and lost with the escaping hydrogen, leading to mass fractionation of the residual atmosphere. Fig. 4 illustrates the mechanism for an atmosphere heated at high altitude by intense EUV radiation. Outflows from a hydrogen-rich atmosphere, consistent with hydrodynamic escape driven by atmospheric heating, have been directly observed during transits of an extrasolar giant planet in close orbit around a solar-type star [50].

Hydrogen escape fluxes high enough to sweep out and fractionate species as heavy as Xe from Earth require energy inputs 2–3 orders of magnitude greater than presently supplied by solar EUV radiation [14]. Observations of young solar-type stars indicate comparable elevations of EUV emission in the first ~50–150 Myr of their evolution toward the main sequence ([14] and references therein). Escape from early Earth could also have been powered by heating of the atmosphere and surface [51,52] by a giant Moon-forming impact [52–55]. Despite earlier suspicions that a pre-existing atmosphere would be completely ejected in the impact event [56], recent modeling suggests that it could largely survive immediate expulsion [57] before escaping more gradually by hydrodynamic outflow.

A Moon-forming collision with Earth probably occurred ~30–50 Myr after solar system origin [10,58].

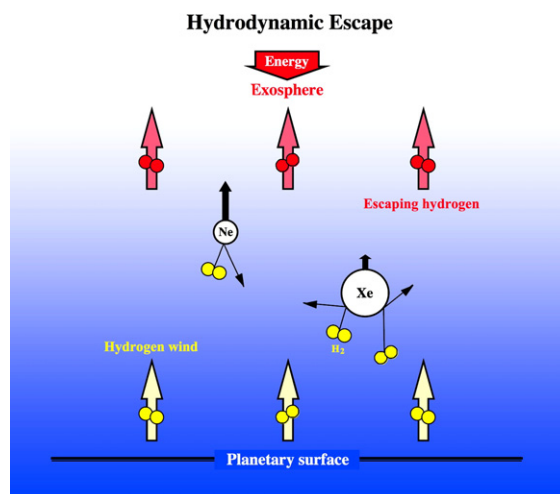


Fig. 4. Hydrodynamic escape in a hydrogen-rich primordial planetary atmosphere, illustrated for input of external energy at high altitudes (the “exosphere”). Exospheric H_2 is heated to escape velocity by adsorption of strong solar EUV radiation or perhaps, on Earth, by frictional drag on material re-entering the atmosphere from an impact-generated, Moon-forming circumplanetary disk [52]. Escaping hydrogen is replenished by rising hydrogen “wind”. Collisions of outward bound H_2 molecules with other atmospheric constituents (illustrated here for Ne and Xe) exert net upward drag forces on them. Equilibrium between this upward drag and gravity leads to an increased average height for these species. However, if the H_2 escape flux is large enough, drag wins for Ne and it is entrained with the escaping H_2 and swept out of the atmosphere; progressively higher fluxes also remove Ar, Kr, and Xe [46]. The importance of hydrodynamic escape, in the context of observed noble gas isotope distributions, is that it can implement loss and fractionation of species as massive as Xe which could not escape “on their own” by classical processes such as Jeans escape [44].

The early Sun likely maintained a high EUV luminosity for only ~50–150 Myr. Thus, with either energy source, conditions favoring hydrodynamic escape were restricted to early epochs in planetary history. Signatures of fractionating escape in atmospheric Ne, Ar, and Kr have since been modified, at least on Earth, by dilution with unfractionated gases degassed from interior reservoirs. Xenon, however, except for isotopes generated by nuclear decay, appears to preserve the composition generated by early escape and is therefore a uniquely powerful recorder of ancient evolutionary histories.

5.2. Xenology

The nine Xe isotopes display records of both physical processing from primordial compositions and, via decay products of the now-extinct radionuclides iodine-129 and plutonium-244, the chronologies of planetary

formation and degassing. Isotopic distributions of this single noble gas, in the Sun, meteorites, and planets, are so richly informative that they have catalyzed a vigorous

subfield of cosmochemical research, called “xenology” by its founder John Reynolds [59].

Terrestrial xenology has two research branches, one concentrating on atmospheric Xe and the other on Xe trapped in the solid Earth. Here the focus is on the atmosphere, specifically on efforts to identify initial compositions and evolutionary mechanisms. Among the many observed or inferred solar-system Xe compositions, the three shown in Fig. 5a are candidates for Xe on the early Earth. The solar wind (SW) composition comes from analyses of Xe implanted by the wind into small grains on lunar and asteroidal surfaces [19] and, in the near future, from the Genesis mission [19,60]. It represents the best estimate of the isotopic distribution in the Sun, by far the largest volatile reservoir in the solar system, and is arguably the most likely composition in the early solar nebula and in bodies that acquired their Xe from it. “Xe–Q” is present in most if not all classes of meteorites, including the most primitive types [61]. The third candidate, U–Xe, is a derived composition obtained by detailed comparison of meteoritic and terrestrial Xe data [62]. It is isotopically identical to SW–Xe except at the two heaviest masses [62,63]. So far U–Xe has not been observed directly in meteorites. It may be present in Jupiter’s atmosphere, but uncertainties in the Galileo Probe measurements [20] are too large to rule between U–Xe and SW–Xe [12]. SW–Xe, Xe–Q, and U–Xe are collectively termed “solar-like” because their isotopic distributions are generally similar to each other and to the Xe believed to be present in the Sun.

All three Xe compositions in Fig. 5a display smoothly mass-dependent elevations of their $^{124-128}\text{Xe}/^{130}\text{Xe}$ isotope ratios compared to Earth. These are the four non-radiogenic isotopes – containing no components produced by nuclear decay – and so the Fig. 5a patterns are direct evidence for generation of these ratios in Earth’s atmosphere by fractionation of a solar-like precursor.

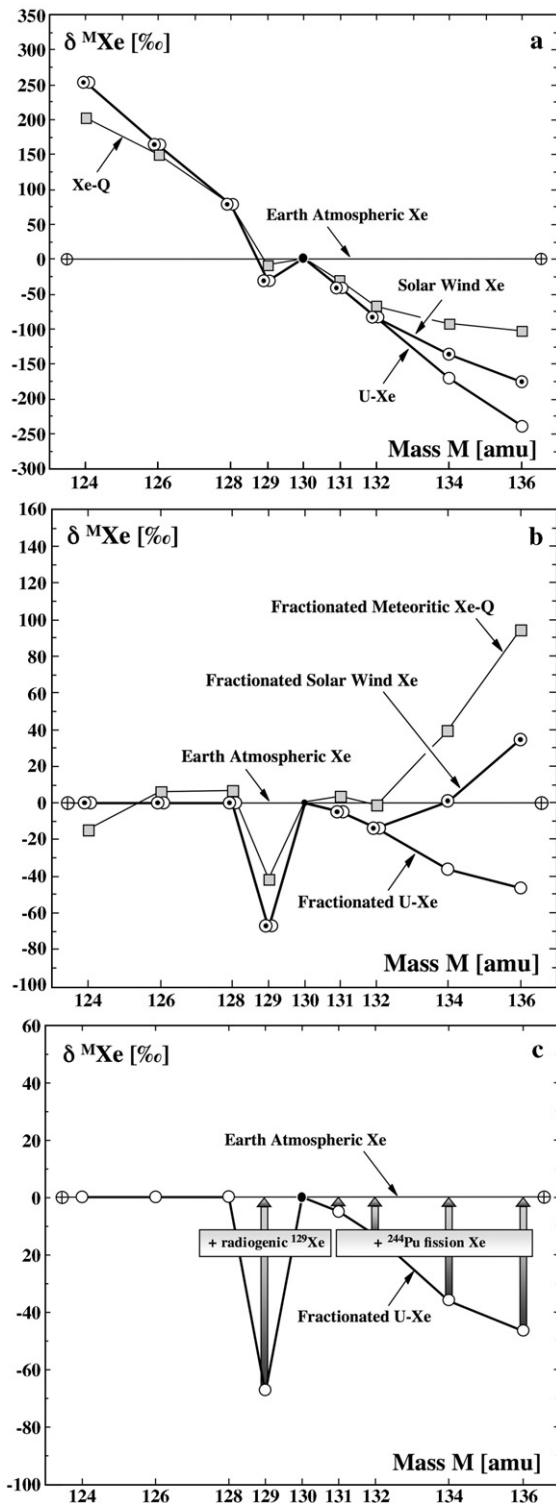


Fig. 5. A time sequence of the evolution of Earth’s atmospheric Xe from primordial (a) to present-day (c) compositions. (a) Compositions of solar wind (SW)–Xe, U–Xe, and meteoritic Xe–Q relative to Xe in Earth’s present atmosphere, plotted as permil differences given by $\delta^M \text{Xe} = 1000 \{ [(^M \text{Xe}/^{130} \text{Xe})_{\text{SW,U,Q}} / (^M \text{Xe}/^{130} \text{Xe})_{\text{air}}] - 1 \}$ ‰. (b) As in (a), but now after fractionation by hydrodynamic escape to the extents needed to best match the terrestrial $^{124-128}\text{Xe}/^{130}\text{Xe}$ isotope ratios. One sees that neither SW–Xe nor Xe–Q can be the primordial precursor of atmospheric Xe since fractionations of these compositions produce overabundances of ^{136}Xe , reflected in $^{136}\text{Xe}/^{130}\text{Xe}$ ratios that are significantly higher than the air value [62]. (c) Post-escape evolution of atmospheric Xe from the residual fractionated U–Xe composition shown in (b) to its present composition. The underabundant isotopes in (b) are augmented by outgassed ^{129}Xe and $^{131-136}\text{Xe}$ generated in Earth’s interior by decay of ^{129}I and ^{244}Pu [26,62].

The observation that parental and present Xe compositions on Earth appear to be related by fractionation was first made 45 years ago in a study of Xe in primitive meteorites [64]. It has since underlain all evolutionary models able to account in at least some respects for contemporary isotopic distributions. The need for a fractionating process applies to any environment in which Earth-like Xe was produced from a solar-like progenitor, on the assembled planet [14,48,65,66] or in pre-planetary planetesimals [66–68].

Fig. 5b shows the Fig. 5a compositions after fractionation by hydrodynamic escape into best agreement with the terrestrial $^{124-128}\text{Xe}/^{130}\text{Xe}$ ratios. The need for U–Xe is now apparent: fractionation of both SW–Xe and Xe–Q generates more ^{136}Xe (and, for Xe–Q, more ^{134}Xe) than Earth’s atmosphere actually contains, and so both are eliminated as candidates for primordial Xe. Fractionated U–Xe, however, does *not* replicate atmospheric Xe throughout; it is underabundant at ^{129}Xe and at the four heaviest isotopes. This brings us back to how the U–Xe composition was obtained. Its derivation rests on three premises: that air Xe contains an outgassed heavy-isotope component produced by fission of an unspecified parent radionuclide within the Earth; that the U–Xe composition exists in primitive meteorites; and that U–Xe and terrestrial Xe are related by mass fractionation. With these assumptions, the derivation yields the U–Xe composition as Earth’s parental Xe, and identifies extinct ^{244}Pu as the dominant source of fission Xe in the atmosphere [62]. (An independent derivation of a differing “U–Xe” composition was carried out by [69]. However this claimed substitute for U–Xe does not give a credible composition for Earth’s atmospheric fission Xe, and is also questionable for other reasons [62].)

Fig. 5c shows the final stage in the modeled evolution of Earth’s Xe to its present state. Hydrodynamic escape dissipates a primordial atmosphere containing U–Xe (Fig. 5a), leaving behind a fractionated U–Xe residual — the initial, non-radiogenic composition of the atmosphere (Fig. 5b). Later outgassing adds isotopes generated by radionuclides trapped within the Earth at its formation, at ^{129}Xe from ^{129}I decay and at $^{131-136}\text{Xe}$ from ^{244}Pu fission.

These two decay products lie squarely at the intersection of the atmospheric and internal branches of xenology. Both have been identified in the Earth’s interior [23,24,26]. Half-lives of their parents are short, 15.7 Myr for ^{129}I and 80.0 Myr for ^{244}Pu [70]. Thus just the presence of excess ^{129}Xe and ^{244}Pu fission Xe tells us that the Earth formed very early, before their parents had decayed away. More than that, the relative abundances of

these radiogenic daughters in and on the Earth today reflect the chronology of major accretional, degassing, and atmospheric escape events in terrestrial history. It seems likely, for example, that the immense energy deposited by a giant Moon-forming impact drove severe outgassing of the interior and loss of volatiles to space. Xe generated by ^{129}I and ^{244}Pu decay up to that time would be removed, re-setting the I–Xe and Pu–Xe chronometers. With different half-lives, these clocks tick at different rates, and the relative abundances of their daughters in the interior and atmosphere can be used to estimate the timing of the impact and the subsequent history of atmospheric Xe (e.g., [26]). The two branches of terrestrial xenology are thus intimately related.

5.3. Modeling earth

Escape from Earth’s primordial atmosphere would have imprinted its signature on atmospheric Kr, Ar and Ne as well as Xe. In fact even larger depletions and isotopic fractionations in these lighter species are expected since they are more readily entrained in the outflowing hydrogen. Many of the basic parameters governing hydrodynamic escape are fixed in its application to Xe fractionation. Compositions of other gases in the residual atmosphere then additionally depend only on species-specific parameters such as masses and isotope ratios in the initial atmosphere [12,14,46].

Results of applying the escape model to Xe, Kr, Ar and Ne in the terrestrial atmosphere are summarized in Fig. 6. Escape in this illustration is driven by energy deposited in a giant impact, but essentially the same results are obtained for hydrogen outflow powered by early solar EUV [14]. Xe evolution from primordial U–Xe, discussed above, is shown in the upper panel; initial isotope ratios for the remaining gases are assumed to be those in the solar wind [19]. The hydrodynamic escape parameters that convert U–Xe to atmospheric Xe over-fractionate Kr and Ar, and so later additions from a second, unfractionated gas source are required to elevate these species to their current compositions. In the Fig. 6 model these are outgassed from a solar-composition interior reservoir acquired during accretion (Section 3).

Neon is more complicated. Isotope ratios generated by escape are higher than atmospheric, and later addition of outgassed solar Ne elevates them further, as seen in the bottom panels. A later episode of energy deposition by a waning solar EUV flux is needed to generate the contemporary $^{20}\text{Ne}/^{22}\text{Ne}$ ratio; here the hydrogen escape flux was intense enough to lift Ne, but not heavier species, out of the atmosphere [48]. EUV-driven fractionation yielding a match to the present

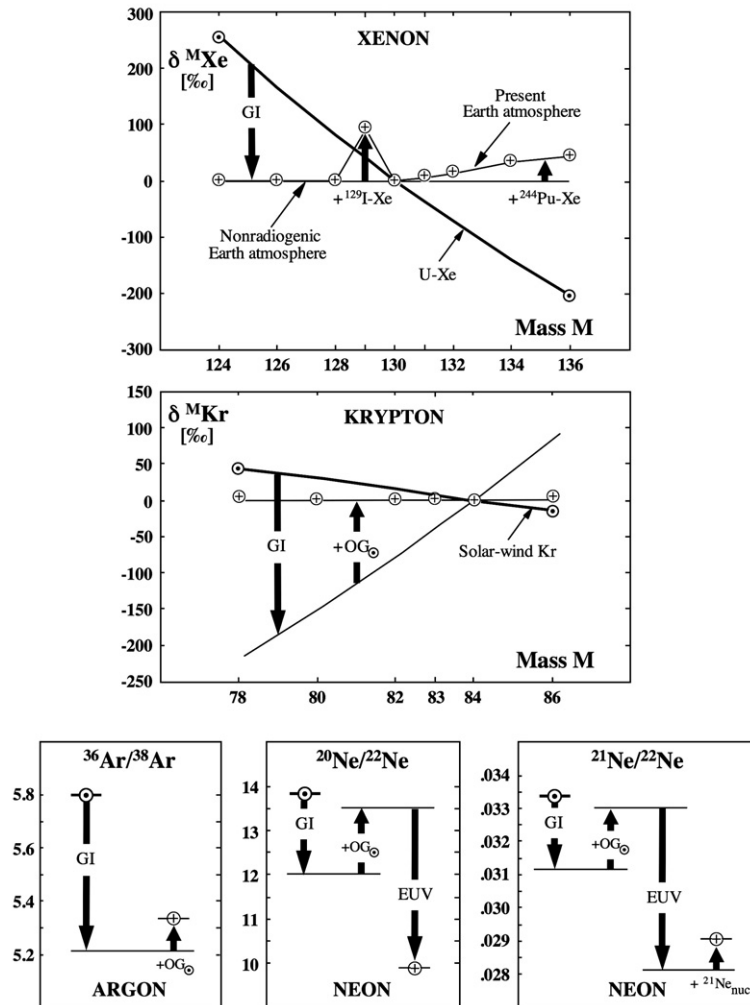


Fig. 6. Evolution of terrestrial Xe, Kr, Ar, and Ne from primordial to present-day isotopic compositions, by giant impact (GI)-driven hydrodynamic fractionation of all the gases, a later stage of solar EUV-powered Ne escape, addition (+OG_⊙) of outgassed solar-composition Kr, Ar, and Ne (but not Xe: see text, Sec. 5.3), and degassing of radiogenic and fissionogenic Xe and crustal nucleogenic ²¹Ne. Degassing of Kr, Ar and Ne could occur at any time after the impact-powered (GI) fractionation. The timing of Ne-only loss (within ~300 Myr [48]) is dictated by the availability of enough solar EUV energy to drive it. Except for this constraint, its ordering relative to OG_⊙ outgassing is not critical; it could occur after outgassing, as in the lower panels, or before. Kr and Xe δ-values are referenced respectively to atmospheric Kr and to nonradiogenic Earth Xe (“fractionated U–Xe” in Fig. 5c). Data from [48].

²⁰Ne/²²Ne ratio slightly over-fractionates ²¹Ne/²²Ne. It is likely, however, that this discrepancy is removed over geologic time by degassed nucleogenic ²¹Ne generated by ¹⁸O(α,n)²¹Ne reactions in the Earth’s crust and mantle [48,71,72].

This evolutionary model accounts reasonably well for isotopic distributions in the terrestrial atmosphere, but at the cost of considerable complexity: two primordial gas reservoirs, one exterior and one interior, and two escape episodes powered by different energy sources at different times early in planetary history. And one of the assumptions seems questionable: why is there

no outgassed Xe, unlike the case for the lighter gases (Fig. 6)? The modeling reason is that the combination of escape over-fractionation plus degassing that replicates the Kr and Ar atmospheric compositions does not work for Xe. Only a trace of solar Xe can be added in this way without perturbing the final Xe ratios beyond their accurately known values. Solar elemental ratios, however, suggest that an amount of Xe much larger than this “trace” should accompany the degassed Kr [14]. Several experimental and theoretical studies have addressed this “missing Xe” problem, in the context of mechanisms that might preferentially sequester Xe in the Earth’s

interior and so make it unavailable for outgassing. One possibility is alloying of Xe and Fe, with transport of the alloy into the core [14]. Results of the first experimental investigation of Xe–Fe alloy formation at deep Earth pressures were negative [73], but recent studies suggest that this may happen in a high-pressure environment if Xe is present at its expected low abundance [74]. There is also experimental evidence for Xe trapping in quartz at lower continental crust pressures by substitution for Si [75]. Formation of solid high-density clusters of Xe atoms in the lower mantle, which then sink into the core, has been proposed [76], although a question here is whether individual atoms could “find” each other and assemble into clusters, given the very low abundance of mantle Xe.

It appears that preferential retention of interior Xe, by one mechanism or another, is not out of the question. Whether or not this occurs is irrelevant, however, in an alternative scenario where degassing, except for radiogenic species, does not contribute significantly to the atmosphere [49]. In this variant of the escape model, the interior source in Fig. 6 is replaced by solar gases carried in accreted cometary ices. If the mixture of escape-fractionated and cometary noble gases is to match the atmosphere, the ices must be characterized by a very low Xe/Kr ratio, essentially the same constraint that applies to degassing. Although some laboratory evidence exists for preferential trapping of Kr relative to Xe in ice at low temperatures [77], direct measurements of cometary noble gases are needed to evaluate models calling for comet contributions to the atmosphere (e.g., [7,49,77]). Analyses of comet dust returned by Stardust [78] will perhaps provide some information, but that mission was not equipped to sample gases evolving from the comet nucleus.

How does nitrogen (Fig. 3) fit into the escape-fractionation model? We can’t answer yet because the isotopic composition of solar-wind N is still unknown. The only direct measurement, by SOHO spacecraft instruments [79], is too uncertain to be useful. There is no consensus on $\delta^{15}\text{N}$ for nitrogen implanted by the wind into lunar samples [80]; two conflicting estimates have emerged from the measurements, one near +40% [81], the other below -250‰ [82,83]. The latter has gained more support because of its compatibility with $\delta^{15}\text{N}$ in Jupiter’s atmosphere [84–86] — a proxy, along with the solar wind, for the Sun and solar nebula. We will see what the Genesis value turns out to be. In the meantime, backward calculations through the noble gas model can be used to estimate what primordial $\delta^{15}\text{N}$ would have to be to generate the present Earth value by escape fractionation. Results suggest an initial $\delta^{15}\text{N}$

within the range shown by the shaded bar in the lower panel of Fig. 3, possibly roughly consistent with the Jovian measurements.

One would think that cometary $\delta^{15}\text{N}$ could be a measure of primordial nitrogen, assuming that these ancient bodies trapped their volatiles from the nebula. But there’s a problem: comets display two different values (Fig. 3), respectively from spectroscopic observations of CN and HCN molecular transitions [87,88]. The negative $\delta^{15}\text{N}$ from HCN is close to other estimates for the solar ratio, and may reflect the N_2 composition in nebular gas. The higher value in CN suggests that CN derives from different parent molecules than HCN, perhaps organic compounds enriched in ^{15}N [87]. The elevated $\delta^{15}\text{N}$ in Titan’s atmosphere [89] might be explained in the same way, although here preferential depletion of ^{14}N by escape fractionation is also a possibility if an energy source sufficient to drive it could be identified on this large and very cold Saturnian satellite. The meteorites complete the roster of solar-system objects with measured $^{15}\text{N}/^{14}\text{N}$ ratios. Their extraordinary range in $\delta^{15}\text{N}$ is due primarily to a wide variety of isotopically distinct sources, many of them in “pre-solar” grains inherited from the molecular cloud from which the solar system formed [90,91].

5.4. Venus and Mars

Modeling the evolution of these two atmospheres is seriously impacted by the absence of critical data, particularly for Venus. Nevertheless, in the context of the Earth model discussed above, something can be said about their probable histories. The relatively weak EUV flux that powered Ne-only loss from Earth (Fig. 6) would have driven escape of Kr and lighter species — but not Xe — from the smaller Venus, and of all the noble gases from the still smaller Mars [12,48]. This loss episode fractionates isotopically solar precursors into good agreement with the limited (Ne and Ar) isotopic data we currently have for Venus [29,48]. Elemental compositions of primordial, pre-escape atmospheres on Earth and Venus, obtained by calculating backwards from present abundances through the escape fractionations, are compared in Fig. 7. Although initial Xe/Ar and Kr/Ar ratios for Venus inherit the large uncertainties in current abundances [14], the agreement of the nominal ratios suggests that both atmospheres evolved — in quite different ways — from similar initial distributions. These primordial atmospheres were probably acquired in the same way from the same reservoir, not surprising for two planets with comparable masses and heliocentric distances. The (unmeasured) isotopic composition of

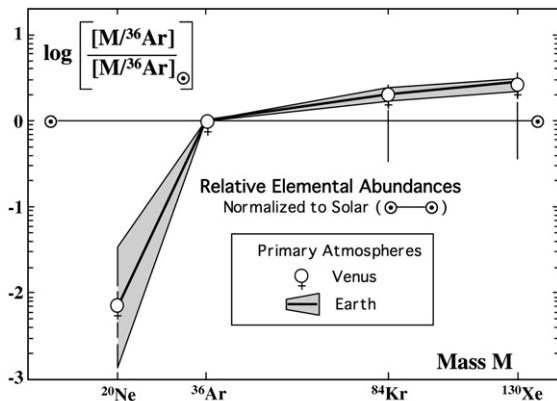


Fig. 7. Modeling results for the elemental compositions of primary atmospheres on Earth and Venus, plotted relative to solar abundance ratios. Shaded regions represent a range of compositions for Earth obtained by variations in the parameters governing giant impact-driven hydrodynamic escape [48].

Venusian Xe should therefore resemble unfractionated U–Xe — an important test of the U–Xe hypothesis.

The noble gas data base for Mars [39] is more complete, thanks to the SNC meteorites. Three processes have emerged from interpretations of these data as probable agents controlling Mars' transition from primordial to present state: hydrodynamic escape and planetary degassing, as on Earth, and, on this much smaller and gravitationally weaker planet, fractionations by sputtering losses [12,40,41,92–94]. It's likely that each of these mechanisms operated most effectively in different epochs of Martian history. During the early period of solar EUV-powered escape, a paleomagnetic field generated by an active core dynamo [95,96] would have shielded the planet from sputtering losses [97]. Later, the dynamo switched off [95], and a dense CO_2 atmosphere may have abruptly collapsed to its present low pressure [98]. Both events would have profoundly altered the course of Martian atmospheric history. With disappearance of the magnetic field, interplay of outgassing with sputtering and photochemical losses from high altitude took control of the subsequent evolution of Ne, N, and Ar [40,41,99,100]. Atmospheric collapse would trigger rapid sputtering removal of pre-existing light gases [41], resulting in present-day compositions that reflect only the action of post-collapse loss mechanisms on gases supplied by outgassing — generating, for example, the large Martian $\delta^{15}\text{N}$ value in Fig. 3. In contrast to Earth and Venus, these species contain no surviving isotopic records of processing by early hydrodynamic escape.

Xenon, however, is so massive and gravitationally concentrated in the lower atmosphere that its abundance is

negligible at the high altitudes of sputtering loss, and so its composition in the total atmosphere is unaffected. Current Xe isotope ratios thus look back through the sputtering era to the earlier epoch of hydrodynamic outflow. They are consistent with escape fractionation of a solar-like primordial precursor, but there are puzzles and ambiguities in current Martian xenology, the latter stemming largely from SNC data that lie right at the edge of the precision needed for quantitative modeling. The principal puzzle is the identity of Xe initially present on Mars, which appears likely to be SW–Xe, not U–Xe [62,101]. Xenon trapped in the Martian interior is also consistent with solar wind [28,102,103]. This points to different provenances for primordial Xe on Earth and Mars.

Fig. 8 compares Mars' atmospheric Xe composition, compiled from SNC meteorite measurements [103], with SW–Xe fractionated to best fit to the data (heavy curve). The match is essentially exact at all isotopes except ^{129}Xe , which lies far above the plot boundary at $\delta^{129}\text{Xe} > 1400\text{‰}$. The atmosphere clearly contains a lot of outgassed radiogenic ^{129}Xe from ^{129}I decay, and therein lies a problem. There is evidence that $^{131-136}\text{Xe}$ produced by ^{244}Pu fission is present in the Martian interior [28,102], and degassing would be expected to carry this into the atmosphere, as on Earth (Fig. 5c). And yet fractionated SW–Xe *by itself* matches the

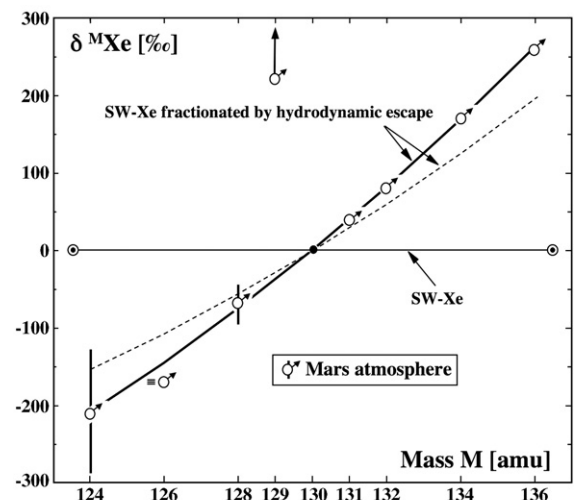


Fig. 8. Mars atmospheric Xe [103] and fractionated SW–Xe, plotted as $\delta^M \text{Xe}$ values as in Fig. 5, but here relative to the composition of SW–Xe. The Mars data are closely matched, except at highly radiogenic ^{129}Xe , by the solar wind fractionation represented by the heavy curve. A weaker fractionation (dashed curve) falls below the Mars points at $^{131-136}\text{Xe}$; in this case addition of ^{244}Pu fission Xe to the fractionated SW–Xe at these isotopes yields a reasonably close fit to the Mars composition. One can see that more precise measurements of the less abundant $^{124-128}\text{Xe}$ isotopes could rule on the presence or absence of fission Xe in the Martian atmosphere.

atmosphere at these isotopes, leaving no room for added fission Xe. The apparent absence of this atmospheric component is difficult to reconcile with the model of Ne, N, and Ar evolution on Mars, which calls for vigorous degassing to balance sputtering losses. One possible solution [101] is a less severe fractionation of SW–Xe, generating the dashed curve in Fig. 8. Now there is room for added contributions at $^{131-136}\text{Xe}$, elevating abundances at these isotopes from the dashed curve by amounts consistent with the ^{244}Pu fission composition. The price paid by the weaker fractionation is a degraded match to the Mars ratios at $^{124-128}\text{Xe}$. These, however, are the rarest Xe isotopes, both the most difficult to measure precisely and those most affected by corrections for non-Martian Xe produced in the SNCs by cosmic-ray-induced nuclear reactions during their journeys from Mars to Earth.

The presence or absence of Pu fission Xe in Mars' atmosphere is an important question because it bears directly on the degassing history of the planet. At the moment the issue is plagued by apparent coincidences. The excellent match of fractionated SW–Xe alone to the Mars data is fortuitous if Pu–Xe is present. If it is absent, the fact that a weaker fractionation plus Pu–Xe fits the data is likewise accidental. The question could be settled by precise measurements of the light isotope ratios. The prospect of obtaining these from the small amounts of atmospheric Xe trapped in some of the SNCs is uncertain. A sample of the atmosphere itself is needed for detailed laboratory study. A Mars sample return mission will certainly include a jug of atmosphere, but it appears that the wait will be long.

6. Summary, and a look ahead

How and from what sources the atmospheres of Earth, Mars and Venus formed, and how they evolved to their present – and very different – states, are classic problems in the planetary sciences. This review has focused on efforts to model evolutionary paths from primordial to current compositions, using available data, mostly on noble gas distributions, as tracers of processing by astrophysically plausible mechanisms.

The status of the field is very different for the three planets. We have what could be called a “standard model” built around escape-fractionation of solar-like primordial atmospheres and planetary degassing. For Earth the model is relatively complete, and it's possible to isolate specific issues for future research. One is the existence of U–Xe, a presumably nebular composition inferred to be present on early Earth but so far not seen directly elsewhere; until it is, it remains hypothetical. A

further challenge to the U–Xe hypothesis is the need to define nebular conditions, spatial or temporal, that could accommodate its presence [63]. A second involves further studies of mechanisms for sequestering Xe in the interior, thus throttling the degassing that would perturb Xe composition generated by hydrodynamic escape. A third and more general issue relates to the coupled histories of atmospheric and interior volatiles. The emphasis here has focused on evolution of atmospheric noble gases, but their origins and histories are not independent of the sources, compositions, and transport mechanisms of gases within the planet. These two volatile systems are linked through their primordial inventories and the geophysical processes of degassing – for example, of ^{129}I and ^{244}Pu decay products – and subduction. Efforts to quantify these links are ongoing (e.g., [23,26]), but are far from complete.

Ultraviolet radiation driving Ne loss from Earth would also have powered escape from Mars and Venus. Signatures of escape fractionation would therefore be expected on all three planets. What we know of Martian atmospheric Xe is consistent with this, although there are ambiguities concerning Pu fission Xe, and the important question of why primordial Xe on Mars appears to be SW–Xe, not U–Xe as on Earth. Histories of the lighter Martian noble gases are not definitive, due partly to unavailable data and partly to complexities in the sputtering mechanism (e.g., [92]) and its dependence, through a paleomagnetic field and possible atmospheric collapse, on Mars' thermal history. Venus is the least documented of the three planets. Here the relevant data base, while sketchy and imprecise, is also consistent with escape fractionation. The prediction that Xe did not escape points to an important test of the U–Xe hypothesis. A modern flight spectrometer sampling the Venusian atmosphere could answer many of the most central questions.

Despite many uncertainties, we have at least a plausible outline of how atmospheric evolution may have proceeded on the terrestrial planets. It's a bit sobering, after 60 years of thought about the problem, to realize that the field has come full circle with its contemporary emphasis on fractionation by escape from gravitational wells. This was just the approach taken by Brown [1] and Suess [2] in accounting for differences between the elemental abundance patterns of solar and terrestrial noble gases. A 1963 review [104] of this early work makes the point: “All but a fraction of about 10^{-7} of the rare gases left the Earth's gravitational field during an early stage of evolution by hydrodynamic outflow without undergoing separation. The rest, however, underwent some process by which a fractionation took place, shifting the abundance ratio (of Ne/Xe) by more than a

factor of 10^4 . A simple explanation for the fractionation of the rare gases is selective loss from a gravitational field during a limited period of time [2].” At that time the theory of mass fractionation in hydrodynamic escape had not been developed, and the appeal was to classical Jeans escape from small pre-planetary planetesimals. Nevertheless this perception of evolutionary processing has a distinctly modern ring.

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