

7 **Origin of Noble Gases in the Terrestrial Planets**

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INTRODUCTION

Identifying the mechanisms that drove the evolution of planetary volatiles from primordial to present-day compositions is one of the classic challenges in the planetary sciences. The field bristles with models of one type or another, but none are without difficulties. Efforts to understand the histories of volatile species in the atmospheres and interiors of the terrestrial planets have concentrated on their noble gases, free of the entanglements of chemical interaction, as evolutionary tracers. The elemental and isotopic compositions of these minor constituents are rich in clues to the chemical characteristics of their source reservoirs, the physics of their evolution, and the nature of the astrophysical and planetary environments in which they evolved. Most workers would agree that atmospheric mass distributions of the nonradiogenic noble gases were probably established very early, through the action of processes operating before, during, or shortly after planetary accretion. But beyond this there are no certainties as yet on the specifics of sources or mechanisms.

The question of past and present volatile inventories on and in the terrestrial planets is intrinsically interesting in the more general context of the evolution of the planets themselves. For each individual body it crosscuts issues relating to atmospheric origin and compositional history, emergence of a coupled atmosphere-surface system and climate evolution, surface morphology and its record of past geological processing, and planetary rheology, differentiation, and degassing history. But the volatile problem extends well beyond its relationship to the initial state of a particular planet and the mechanisms that drove it down its specific evolutionary track. Attempts to decipher planetary histories in the broader context of the evolution of the solar system as a whole are focusing more and more attention on the sources and processing of volatiles in the primordial solar accretion disk, in primitive meteorites, and in the terrestrial planets as a class.

One of the salient characteristics of the composition of the Earth is the depletion in volatiles compared to the parental solar nebula relative abundances. This is most pronounced in the noble gases (Fig. 1). However, the acquisition by the planet of these unreactive elements at even these levels pose considerable problems. A comparison between noble gases on the terrestrial planets and other solar system objects reveals significant differences in both elemental ratios and isotopic compositions and indicate that complex processes were involved in sequestering planetary volatiles from the nebula, as well as providing important indications of the sources and evolutionary history of planetary volatiles. Also, noble gas isotope inventories that are produced by nuclear

processes within the planets are clearly identified against the strong depletion of primordial nuclides, and provide both chronological information about volatile retention on the planets and the extent of mantle degassing. While considerations of the origin of planetary noble gases have been predominantly focused on those presently found in the atmosphere, noble gases still within the Earth provide further constraints about volatile trapping within the planet during formation. A wide range of noble gas information for the Earth's mantle has been obtained from mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). This indicates that separate reservoirs within the Earth were established early in Earth history that have characteristics that are distinct from those of the atmosphere, and demand inclusion in comprehensive models of Earth's volatile history. Planetary probes sent into the atmospheres of Venus and Mars have provided data to formulate model histories for these planets as well. Some clues to the interior composition of Mars are even available from Martian meteorites. Therefore, the evolution of Earth volatiles can be considered within the context of terrestrial planet formation across the solar system.

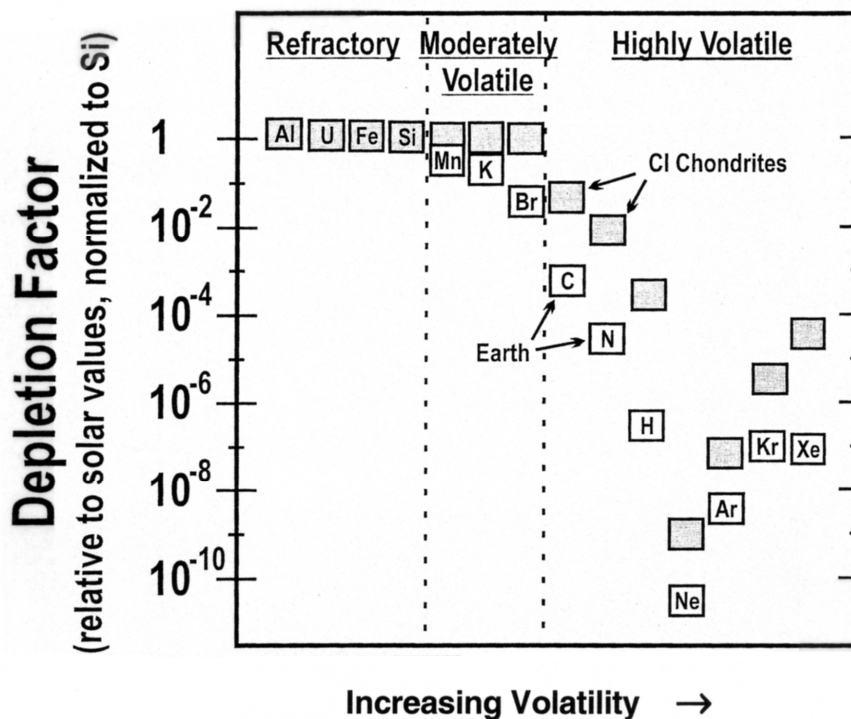


Figure 1. Compared to solar relative abundances, elemental abundances on the Earth show a general trend of increasing depletion with volatility, with noble gases amongst the most highly depleted. CI chondrites are not depleted in moderately volatile elements, but also show strong depletion in highly volatile elements. Data from Anders and Grevesse (1989), Wasson and Kallemeyn (1988), and McDonough and Sun (1995).

The origins of the noble gas features of the terrestrial planet atmospheres and interiors have defied simple explanations, and so a number of different models have been proposed for volatile sources and modification processes. These have often expanded in complexity as additional constraints have emerged, but all models still have problems. The relevant data for noble gases in the atmospheres and interiors of the terrestrial planets, and the constraints these provide, are summarized below. The presently observed volatile states of the planets are the result of acquisition processes that reflect the sources

of noble gases and associated fractionations, followed by losses from the planets that included modification of the composition of residue species. Acquisition and loss processes are discussed separately below, although models that are consistent with the available data include elements of both aspects.

The discussions here are necessarily based on conclusions of more detailed evaluations of available data. More information can be found in this volume in the reviews of terrestrial noble gases (Graham 2002), of models for terrestrial degassing (Porcelli and Ballentine 2002), of solar and planetary characteristics (Wieler 2002), of Mars (Swindle 2002), and of meteorites (Ott 2002). For earlier reviews or alternative viewpoints on the origin of planetary volatiles, see, e.g., Lewis and Prinn (1984), Ahrens et al. (1989), Pepin (1991, 1992, 1994, 1997), Jakosky et al. (1994), Hutchins and Jakosky (1996), and Ozima and Podosek (2001).

CHARACTERISTICS OF PLANETARY NOBLE GASES

The primary references for comparing noble gases are those of the solar nebula, generally represented now by solar gases. Compared to these noble gases, those in the atmospheres of the terrestrial planets show strong elemental and isotopic fractionations. These provide the primary constraints on models of the origin of planetary noble gases, and are reviewed below.

Planetary noble gas abundance patterns

Noble gas abundances in terrestrial planetary atmospheres relative to the solar composition (which represents that of the primordial solar nebula) are shown in Figure 2, along with the pattern exhibited by trapped noble gases in bulk chondrites. Helium is lost from the planetary atmospheres to space, and is not included here. All objects have a striking depletion in noble gases relative to solar abundances (normalized to Si). Chondrites display a regular pattern across the noble gases, with the lightest noble gases displaying the greatest depletions. Although the mechanisms of noble gas trapping are not understood (as discussed further below), this pattern seems consistent with the generally greater retentivity of the heavier noble gases. The Ne/Ar ratios of the terrestrial planets and chondrites are similar, with normalized abundances varying by 10^3 , from gas-rich Venus to gas-poor Mars. The heavier noble gases display greater variations in relative abundances. While the Kr/Ar ratios of chondrites and the Earth are similar, the terrestrial Xe/Kr ratio is much lower. The difference was initially thought to be due to the sequestration of terrestrial Xe in other terrestrial reservoirs. However, investigations of possible reservoirs of Xe, such as shales or glacial ice, failed to find this “missing Xe” (Bernatowicz et al. 1984, 1985; Wacker and Anders 1984; Matsuda and Matsubara 1989). The lower terrestrial Xe/Kr ratio has since usually been considered a feature of the Earth (see, however, Ozima and Podosek 1999 and Rayleigh distillation section below). Although relative abundances in chondrites were historically called the “planetary pattern” based on similarities with the Earth’s atmosphere, and this in turn drove the search for the “missing Xe”, it is now clear that these trapped meteoritic gases do not have such direct relevance to the planets, and so are no longer properly termed “planetary”. However, the reason why the Earth does not exhibit a systematic depletion pattern relative to solar gases (Fig. 2) still requires explanation.

The pattern exhibited by Mars closely follows that of the Earth, with a near-solar Xe/Kr ratio. The available data for Venus likewise suggest solar-like Xe/Kr, although uncertainties are large. Despite these uncertainties, however, it seems clear that Venus differs markedly from the other two terrestrial planets in having an Ar/Kr ratio that is also close to solar.

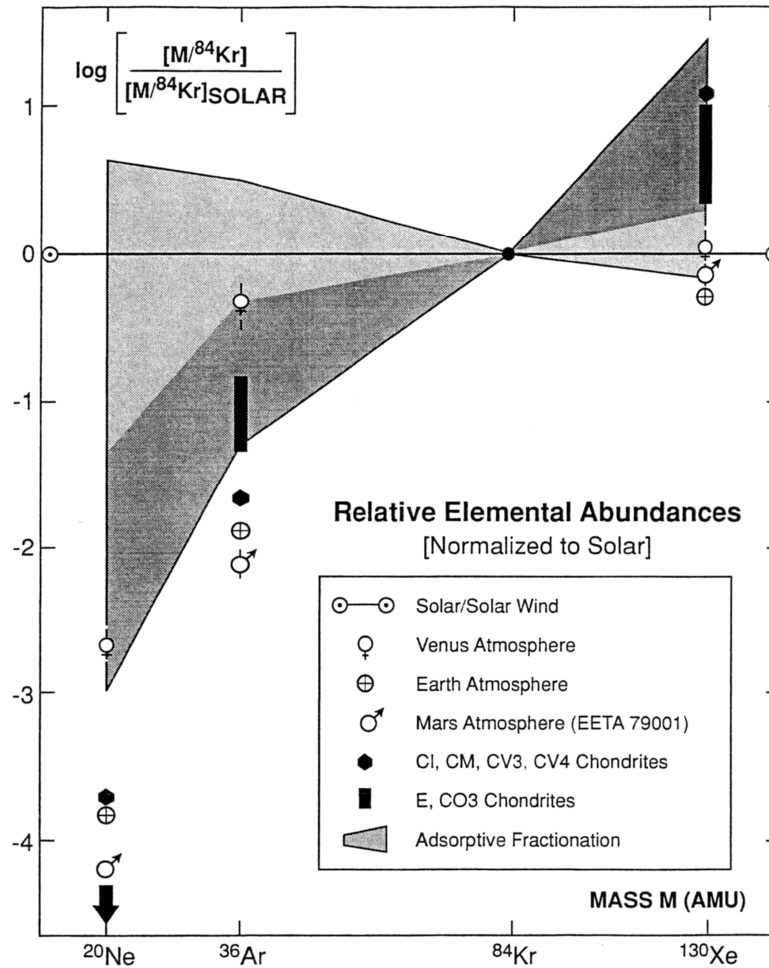
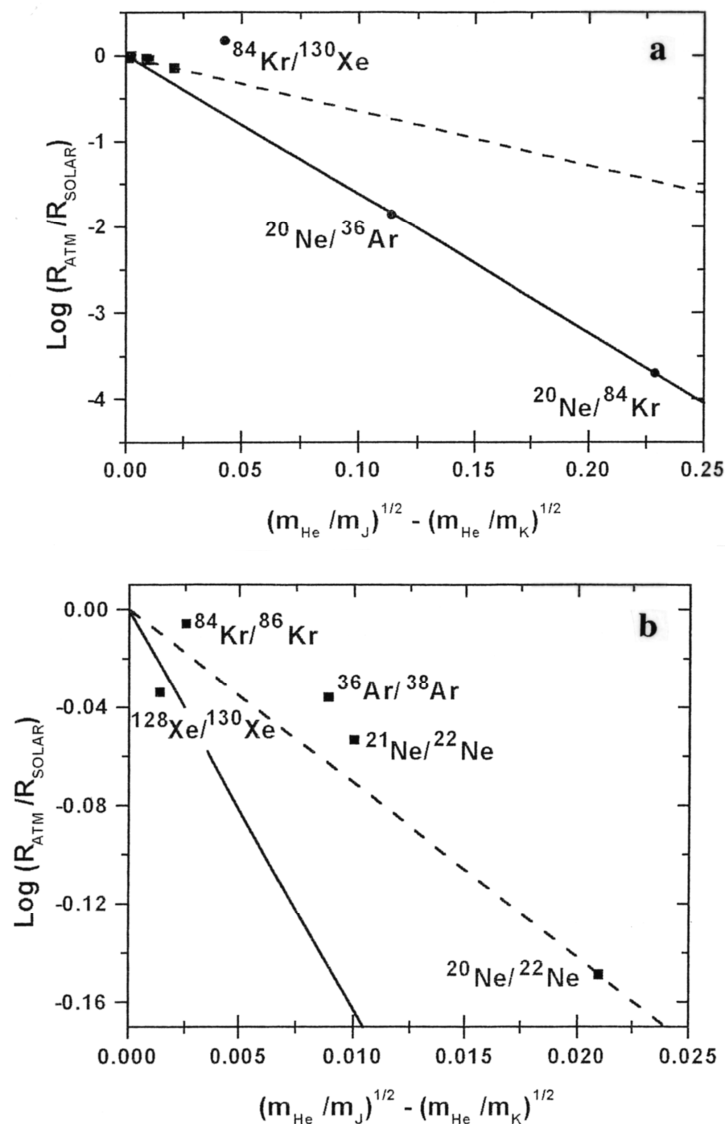


Figure 2. Noble gas $M/^{84}\text{Kr}$ abundance ratios in terrestrial planet atmospheres and volatile-rich meteorites, plotted with respect to solar relative abundances and compared to the range of elemental fractionations (with respect to ambient gas-phase abundance ratios) determined from laboratory adsorptive experiments and from analyses of natural sedimentary materials (Pepin 1991). These fractionations generally fall in the darker shaded area of the figure, except for a number of measurements on carbon black (Wacker 1989) displaying the smaller or reversed patterns within the lighter shading. Data from references cited in the text and in Pepin (1991).

Rayleigh distillation and planetary noble gases. It has been suggested that the abundance pattern of trapped “Q-phase” noble gases—the most abundant and widely distributed primordial component in meteorites (Wieler 1994; Busemann et al. 2000; Ott 2000)—displays characteristics that are compatible with derivation by Rayleigh distillation of solar gases (Pepin 1991; Ozima et al. 1998). The Ozima et al. model, which assumes distillation of the entire nebular gas phase, was extended to the derivation of the terrestrial noble gases by Ozima and Podosek (1999) and Ozima and Igarashi (2000). Their arguments, if valid, would suggest that a distillation process other than hydrodynamic escape should be seriously considered in scenarios for the origin of terrestrial noble gases. If a well-mixed nebular reservoir that initially contains solar gases is progressively depleted by relative escape rates that are inversely proportional to the square root of mass, as assumed in the model, then a linear relationship is expected between the parameters shown in Figure 3. Several observations can be made here. There are two relative abundance ratios, $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{36}\text{Ar}/^{84}\text{Kr}$, that fall on a straight line that

**Figure 3.**

(a) Rayleigh distillation of initially solar noble gases in the nebula, with the escape rate of each species inversely proportional to the square-root of its mass, will produce fractionations between any isotopes j and k that fall along a straight line in this plot. The solid line is fit through two of the three independent terrestrial noble gas ratios representing relative elemental abundances.

(b) Isotopic ratios fit poorly around a line (dashed). Note that the solid line for elemental ratios and the dashed line for isotope ratios do not fit all the data, and do not coincide with one another, indicating that this mechanism has not controlled any of the observed terrestrial noble gas characteristics.

passes through the origin. Note that other ratios that involve these same elements, such as $^{20}\text{Ne}/^{84}\text{Kr}$, are not independent and so necessarily fall on the same line (Ozima and Podosek 1999). The $^{20}\text{Ne}/^{130}\text{Xe}$ ratio does not fall on the correlation; Ozima and Podosek (1999) argue that Xe has been either preferentially lost or hidden, although it is not clear how Xe could have been lost preferentially to the lighter noble gases, nor why any hidden Xe has not been found. Isotopic ratios of the atmosphere also do not fall on the correlation. While these may have been affected by other modification processes, strong isotopic fractionations generated by mass-dependent loss will necessarily modify elemental ratios. For Mars, a similar pattern is evident. The relative abundances of Ne, Ar, and Kr fall on the correlation, while neither Xe nor any of the isotopic compositions do. In sum, only 2 out of 3 elemental ratios and none of the isotopic compositions fall are compatible with the nebular Rayleigh distillation hypothesis; moreover there is no known astrophysical mechanism for the required distillation of the entire nebula. Therefore, adopting nebular Rayleigh distillation as an alternative to local processing by mechanisms such as hydrodynamic loss (see below) from individual planets leads to more features that require separate explanation than those that are easily explained. There

are also mechanisms other than nebular distillation that could have been responsible for generating the meteoritic Q-gases. Fractionation by hydrodynamic blowoff of compositionally solar-like transient atmospheres degassed from primitive planetesimals can yield close matches to meteoritic isotopic data for Xe, Kr, Ar and Ne, and Q-phase elemental ratios can be reproduced in this model by adsorption of residual atmospheric gases on planetesimal surface grains with reasonable choices for gas-solid distribution coefficients in the adsorptive process (Pepin 1991, 2002).

Terrestrial noble gases

Primordial He in the upper mantle. The first clear evidence for the degassing of primordial volatiles from the solid Earth came from He isotopes. The isotopic composition of He in the atmosphere provides a reference, with a $^3\text{He}/^4\text{He}$ ratio of $R_A = 1.4 \times 10^{-6}$. However, it has no significance for the origin of volatiles in the Earth, since He has an atmospheric residence time of only ~ 1 Ma before being lost to space, and an isotopic composition that is the result of a variety of sources for both isotopes (see Torgersen 1989). Radiogenic He is primarily ^4He , with a ratio of $^3\text{He}/^4\text{He} \sim 0.01 R_A$ (Morrison and Pine 1955), and in the absence of initially trapped He would define the mantle composition. However, measurements at mid-ocean ridges found that He in mantle-derived mid-ocean ridge basalts (MORB) has $^3\text{He}/^4\text{He}$ ratios substantially greater than that of the atmosphere (Clarke et al. 1969; Mamyrin et al. 1969), with an average of $8 R_A$ (see Graham 2002). Therefore, mantle He contains ‘primordial’ He trapped during Earth formation and with a high $^3\text{He}/^4\text{He}$ ratio. The ratio of $^3\text{He}/^4\text{He} = 120 R_A$ for the Jupiter atmosphere (Mahaffy et al. 1998; see Wieler 2002) provides the best estimate for the solar nebula ratio and is often taken as the initial value for the Earth. The solar wind value of $330 R_A$ deduced from lunar soil measurements by Benkert et al. (1993) and Palma et al. (2002)—which agrees within error with the SW- $^3\text{He}/^4\text{He}$ ratio of $290 \pm 55 R_A$ measured by SOHO spacecraft instruments (Bodner and Bochsler 1998; see Wieler 2002, this volume)—was established after D burning in the Sun, and is the correct initial Earth value if terrestrial He was derived from solar wind implantation on accreting materials (Podosek et al. 2000) rather than directly from the nebula. Lower values for the mantle are due to radiogenic He production. Unfortunately, due to the ubiquity of parent U and Th, initially trapped and subsequently unaltered He has not been found to provide direct evidence for the initial terrestrial isotopic composition.

Upper mantle He abundance. The mantle sampled by MORB has a relatively uniform isotopic composition, and so a relatively constant proportion of trapped He. Early models for the distribution of noble gases in the mantle identified this reservoir as the upper mantle above the 670-km seismic discontinuity (e.g., Allègre et al. 1983). However, there is now evidence that there is no boundary to convection at this depth (e.g., Helffrich and Wood 2001; van Keken et al. 2002), although the extent of the MORB source reservoir is still debated (see Porcelli and Ballentine 2002, this volume, for discussion). The concentrations in the upper mantle reservoir are highly depleted due to degassing to the atmosphere. At present, available data suggests that there is $(1.2\text{--}4.6) \times 10^9$ atoms $^3\text{He}/\text{g}$ and $(1.4\text{--}5.4) \times 10^9$ atoms $^{20}\text{Ne}/\text{g}$ (see Porcelli and Ballentine 2002, this volume) in the MORB source. The amount that was originally incorporated there can be obtained only if the amount that has degassed and the reservoir volume are assumed. For example, if all of the atmospheric ^{20}Ne were degassed from 25% of the mantle (i.e., the volume above a depth of 670 km), then there was originally 1.75×10^{12} atoms $^{20}\text{Ne}/\text{g}$ in that volume. However, this does not consider losses to space, nor sources that added volatiles directly to the atmosphere.

Primordial He in the deep Earth. The $^3\text{He}/^4\text{He}$ ratios measured in ocean island basalts (OIB) are more variable, with values both below and above those of MORB.

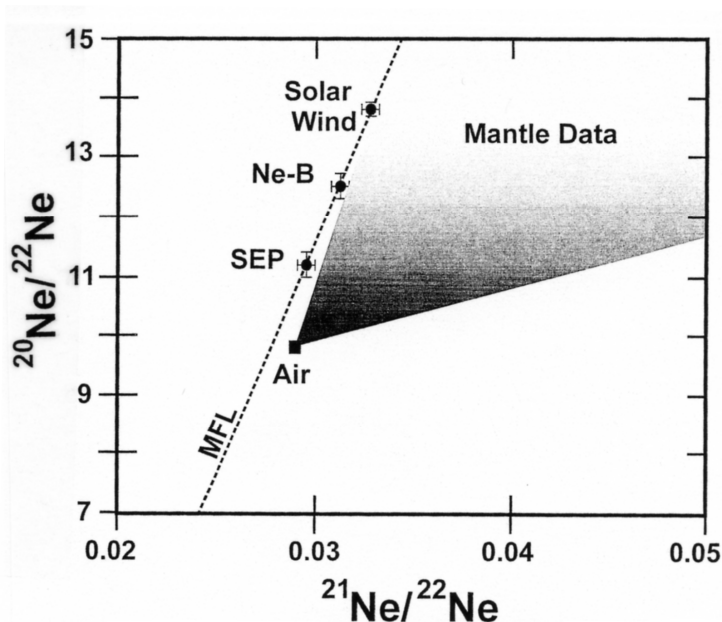
$^3\text{He}/^4\text{He}$ values below MORB are often associated with basalts containing Pb isotopes more radiogenic than MORB, and probably include recycled components (e.g., Kurz et al. 1982; Hanyu and Kaneoka 1998). More significant for the origin of noble gases in the Earth are the OIB with higher values that require at least one mantle component with a time-integrated $^3\text{He}/(\text{U}+\text{Th})$ ratio greater than that of the MORB-source mantle (Kurz et al. 1982; Allègre et al. 1983). This component must have a ratio at least as high as the values of 32-38 R_A measured in Loihi Seamount, the youngest volcano in the Hawaiian Island chain (Kurz et al. 1982), and Iceland (Hilton et al. 1999). It is likely that this component has been stored somewhere below the upper mantle in order to have avoided degassing and homogenization, although the nature of the reservoir is currently debated (see Porcelli and Ballentine 2002, this volume). It has been argued that the high $^3\text{He}/^4\text{He}$ component represents mantle that has remained undegassed since Earth formation. Assuming that this contains a bulk silicate Earth U concentration of 21 ppb and Th/U = 3.8, along with an initial value of $^3\text{He}/^4\text{He} = 120\text{-}330 R_A$ and a present value of 38 R_A , then the reservoir has $(6.1\text{-}7.9) \times 10^{10}$ atoms $^3\text{He}/\text{g}$. If losses of He had occurred, the initial He concentration of this reservoir would have been greater. This provides an important constraint on the amount of He that must have been trapped within the mantle. It should be emphasized that this calculation does not make any assumptions regarding the volume or location of this reservoir in the mantle, issues that are presently contentious (see Porcelli and Ballentine 2002). Nevertheless, the presence of such a reservoir anywhere in the mantle requires that such concentrations were trapped in at least some portion of the mantle.

One alternative interpretation of the high $^3\text{He}/^4\text{He}$ ratios is that it represents He from the core. While this idea remains speculative, partitioning sufficient He into the core also requires high He concentrations into the mantle during core formation (Porcelli and Halliday 2001). The amount of He is uncertain and depend upon the conditions of core formation, but concentrations of He trapped within the mantle as high as $(0.6\text{-}70) \times 10^{11}$ atoms ^3He may be required (Porcelli and Halliday 2001). It has also been suggested that the source has a high $^3\text{He}/(\text{U}+\text{Th})$ ratio due to greater depletion of U and Th than He (Graham et al. 1990; Helffrich and Wood 2001). This is possible if U and Th are more incompatible than He, which has not been demonstrated experimentally. Other difficulties in using this as a basis for a model for all the noble gases also have not been worked out (see Porcelli and Ballentine 2002, this volume, for further discussion). Alternatively, it has been argued that high $^3\text{He}/^4\text{He}$ ratios are from a reservoir that is depleted, rather than gas-rich, due to preferential removal of U relative to He (Graham et al. 1990; Anderson 1998; Helffrich and Wood 2001). This model is difficult to assess (see Porcelli and Ballentine 2002), but likely also requires high He concentrations as a starting condition so that sufficient He remains after depletion.

Atmospheric Ne. Ne isotopic compositions for the atmosphere and solar system reservoirs are summarized in Pepin (1991) and are shown in Figure 4. The greatest differences between solar system bodies are seen in the $^{20}\text{Ne}/^{22}\text{Ne}$ ratios. The value of $^{20}\text{Ne}/^{22}\text{Ne} = 13.8 \pm 0.1$ (Benkert et al. 1993; Pepin et al. 1995) derived for the solar wind is believed to represent the initial solar nebula composition. Meteorites have a variety of components. Ne isotope ratios in bulk CI chondrites scatter around an average $^{20}\text{Ne}/^{22}\text{Ne}$ of 8.9 ± 1.3 . The meteoritic Q-component (Wieler 1994), sited in the surfaces of carbonaceous phases in primitive meteorites and possibly derived by fractionating processes operating on parent bodies (Pepin, 1991) or in the solar nebula itself (Ozima et al. 1998), and thought to be relatively free of 'exotic' components, has $^{20}\text{Ne}/^{22}\text{Ne} = 10.1$ to 10.7 (Busemann et al. 2000). The terrestrial atmospheric ratio of 9.8 can be derived either from mixing meteorite and solar components or by fractionation of solar Ne. The difference between the solar (0.033) and atmospheric (0.029) $^{21}\text{Ne}/^{22}\text{Ne}$ ratios is

consistent with fractionation of solar Ne and addition of radiogenic ^{21}Ne (see Porcelli and Ballentine 2002, this volume).

Figure 4. The Ne isotope composition of terrestrial reservoirs, compared to Ne from solar wind, solar energetic particle (SEP), and Ne-B (a meteoritic composition from irradiation of solar wind and SEP). The atmosphere can be derived from fractionation of solar Ne, with the addition of nucleogenic ^{21}Ne produced within the Earth. Mantle compositions have greater $^{20}\text{Ne}/^{22}\text{Ne}$ ratios, due to the presence of unfractionated solar Ne within the Earth, and greater $^{21}\text{Ne}/^{22}\text{Ne}$ ratios due to addition of nucleogenic ^{21}Ne . See compilations by Busemann et al. (2000) for extraterrestrial data and Graham (2002, this volume) for mantle data. MFL is the fractionation line for mass-dependent Rayleigh distillation losses.



Solar Ne within the Earth. Samples from the Earth's mantle have measured $^{20}\text{Ne}/^{22}\text{Ne}$ ratios that are greater than that of the atmosphere, and extend toward the solar value (Fig. 4). Since these isotopes are not produced in significant quantities in the Earth, this is unequivocal evidence for storage in the Earth of at least one nonradiogenic mantle component that is distinctive from the atmosphere and was trapped during formation of the Earth. This component must have a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio at least as high as the highest measured mantle value, with lower measured ratios due to addition of contaminant air Ne. A few of the mantle $^{20}\text{Ne}/^{22}\text{Ne}$ ratios approach the solar wind value of 13.8, which is also assumed to represent the solar nebula, although most are lower. The solar wind/nebular ratio has commonly been taken to be that of the mantle. Recently, however, it has been suggested that OIB and MORB data indicate that the isotopically light component in the mantle is actually Ne-B (Trieloff et al. 2000, 2002; Ozima and Igarashi 2000), which is a mixture of solar wind and solar energetic particle (SEP) Ne. Ne-B has a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of about 12.5 (Black 1972), significantly below the solar value. The few measured mantle values above this (Sarda et al. 1988; Hiyagon et al. 1992) were insufficiently precise to firmly establish the presence of Ne with a higher value. This raises the possibility that mantle Ne was supplied by planetary accretion of planetesimals carrying Ne-B (Trieloff et al. 2000, 2002). However, recent analyses for Icelandic OIB samples found $^{20}\text{Ne}/^{22}\text{Ne} = 13.75 \pm 0.32$ (Harrison et al. 1999), demanding the presence of solar Ne in the mantle, although the validity of this value is debated (Trieloff et al. 2000, 2001; Ballentine et al. 2001). It should be noted that it is possible that isotopic fractionation processes have modified Ne in mantle-derived samples during transport and degassing, but there is no information available to rigorously evaluate this.

The only other solar system composition with $^{20}\text{Ne}/^{22}\text{Ne}$ ratios greater than that of the atmosphere is Q-Ne with $^{20}\text{Ne}/^{22}\text{Ne} = 10.7$ (Fig. 4). Recently, Ozima and Igarashi (2000) argued that there is a preferential grouping of both MORB and OIB data at the intermediate value of $^{20}\text{Ne}/^{22}\text{Ne} = 10.8$, and suggested that this was due to the presence of Q-Ne in the mantle. This would demand mechanisms for the trapping and preservation of

yet another interior component. Moreover, Q gases have ${}^3\text{He}/{}^{22}\text{Ne} \sim 0.14$ (Busemann et al. 2000); all MORB and OIB ${}^3\text{He}/{}^{22}\text{Ne}$ values are at least an order of magnitude greater (see below), and so this cannot be a Ne component in the mantle unless prior strong elemental fractionation has occurred. It should be noted that the statistical arguments for such a component are weak and do not account for the common observation that intermediate ${}^{20}\text{Ne}/{}^{22}\text{Ne}$ ratios commonly reflect some atmospheric contamination that is only partly resolved by step-heating. Without additional support, this hypothesis does not warrant further consideration.

Mantle He/Ne ratios. The MORB He and Ne isotopic compositions can be used to calculate the ${}^3\text{He}/{}^{22}\text{Ne}$ ratio of the source region prior to any recent fractionations created during transport and eruption. Since ${}^4\text{He}$ and ${}^{21}\text{Ne}$ production rates are directly coupled, ${}^3\text{He}/{}^4\text{He}$ and ${}^{21}\text{Ne}/{}^{22}\text{Ne}$ isotope variations should be correlated (see Porcelli and Ballentine 2002, this volume). A review of available Hawaii and MORB data (Honda and McDougall 1998) found a mantle average of ${}^3\text{He}/{}^{22}\text{Ne} = 7.7$. This is greater than the most recent estimate of 1.9 for the solar nebula (see discussion in Porcelli and Pepin 2000), and so requires some elemental fractionation of incorporated light solar noble gases. There is evidence that this value may not be uniform in the mantle, although it has not been conclusively established that more than one component was trapped in early Earth history and preserved since then (see Porcelli and Ballentine 2002 for further discussion).

Ar in the atmosphere. The initial ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratio in the solar system is $\sim 10^{-4}$ to 10^{-3} (Begemann et al. 1976). The atmosphere has ${}^{40}\text{Ar}/{}^{36}\text{Ar} = 296$, so that essentially all the ${}^{40}\text{Ar}$ has been produced by ${}^{40}\text{K}$ decay. The atmospheric ${}^{38}\text{Ar}/{}^{36}\text{Ar}$ ratio of 0.188 is similar to that found in CI chondrites of 0.189 ± 0.002 (Mazor et al. 1970) but substantially higher than the current estimate of 0.173 for solar wind (Pepin et al. 1999; Palma et al. 2002). Atmospheric Ar derived from a solar source therefore must have been fractionated.

Radiogenic ${}^{40}\text{Ar}$. A measure of the extent of mantle degassing can be obtained from the K- ${}^{40}\text{Ar}$ budget. The concentration of K in the bulk silicate Earth is generally estimated to be 270 ppm K, which has produced 2.4×10^{42} atoms ${}^{40}\text{Ar}$. Therefore, 41% of the ${}^{40}\text{Ar}$ that has been produced is now in the atmosphere (Allègre et al. 1986, 1996; Turcotte and Schubert 1988), and a significant reservoir of ${}^{40}\text{Ar}$ remains in the Earth. It should be noted that there has been some debate regarding the terrestrial K content (Albarède 1998; see Porcelli and Ballentine 2002, this volume, for discussion), and a downward revision could require a substantially greater degassing efficiency for the Earth. It has sometimes been assumed that the mantle reservoir that is rich in ${}^{40}\text{Ar}$ is the same as that with high ${}^3\text{He}/{}^4\text{He}$ and so is rich in ${}^3\text{He}$, although this is not the case of all mantle models (see Porcelli and Ballentine 2002).

Solar Ar in the mantle? Measurements of MORB and OIB ${}^{38}\text{Ar}/{}^{36}\text{Ar}$ ratios typically are atmospheric within error, but have been of low precision due to the low abundance of these isotopes (Fig. 5). While some high precision analyses of MORB and OIB samples have found ${}^{38}\text{Ar}/{}^{36}\text{Ar}$ ratios lower than that of the atmosphere (Valbracht et al. 1997; Niedermann et al. 1997), others did not (Kunz 1999). Pepin (1998) argued that the low values are due to mantle components with solar light isotopes. The unambiguous identification of solar Ar in the mantle clearly would have important implications for the origin of terrestrial noble gases, and additional analyses are required to firmly establish whether there are mantle samples that contain non-atmospheric ${}^{38}\text{Ar}/{}^{36}\text{Ar}$ ratios not masked by air Ar contamination. However, atmospheric ratios in the mantle could be explained either by early trapping of Ar that had been fractionated or subduction of atmospheric Ar (see Porcelli and Wasserburg 1995b).

Kr isotopes. Solar, bulk meteorite, and terrestrial Kr isotopic compositions (Fig. 6)

seem to be generally related to one another by mass fractionation (see Eugster et al. 1967; Pepin 1991), with the atmosphere depleted in light isotopes by $\sim 0.8\%$ /amu relative to the solar composition (Pepin et al. 1995). Atmospheric Kr (“Air Kr”) is precisely related to the solar composition by mass fractionation; a similarly good fit to terrestrial isotope ratios is generated by mixing of severely fractionated solar Kr with degassed solar Kr, as discussed later in the section “Hydrodynamic escape”. Meteoritic Kr is also generally consistent within error with fractionated solar Kr, but with a possible excess in ^{86}Kr . Mars Kr, in contrast, is solar-like (Wieler 2002; Swindle 2002, both this volume).

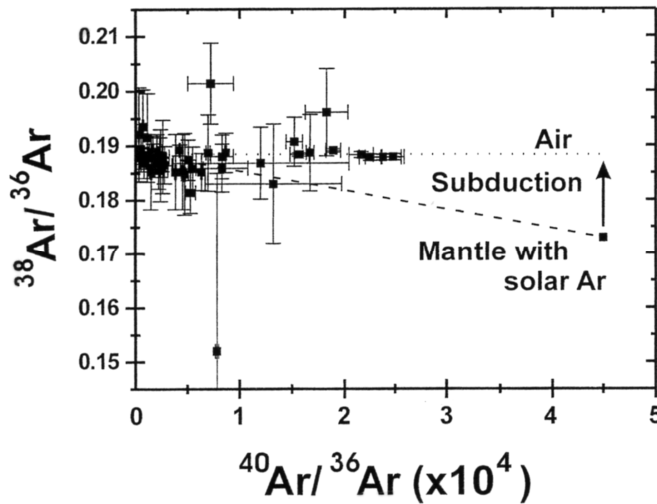
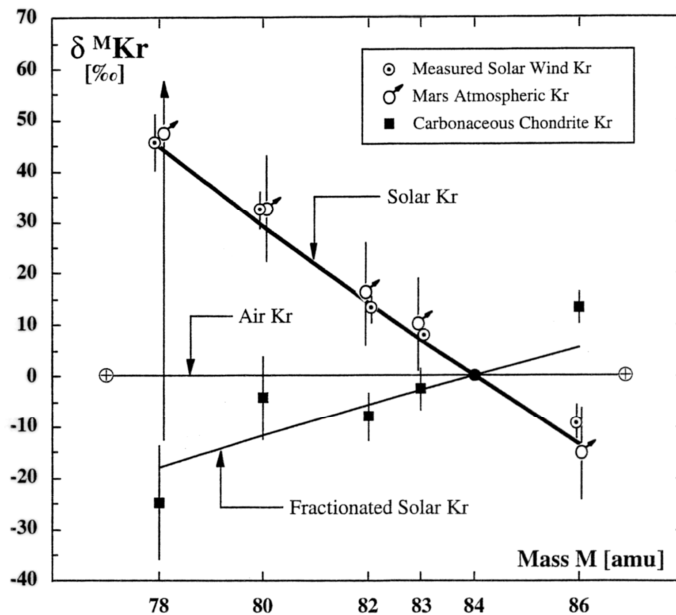


Figure 5. The $^{38}\text{Ar}/^{36}\text{Ar}$ ratio of mantle-derived volcanics are generally within error of the atmosphere, while $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are much greater due to addition of radiogenic ^{40}Ar . A mantle component with a solar $^{38}\text{Ar}/^{36}\text{Ar}$ ratio falls outside the array of data, indicating that non-radiogenic mantle Ar was initially trapped after fractionation from the solar composition, or is dominated by Ar subducted after atmospheric fractionation. Data are from Sarda et al. (1985), Hiyagon et al. (1992), Honda et al. (1993), Niedermann et al. (1997), and Kunz (1999).

Figure 6. Krypton isotopic compositions in solar-system volatile reservoirs, plotted as permil deviations from the $^{M}\text{Kr}/^{84}\text{Kr}$ ratios in terrestrial air (Basford et al. 1973). The heavy “Solar Kr” curve represents a smooth fit to the measured solar-wind isotope ratios. Measured solar wind Kr from Wieler and Baur (1994) and Pepin et al. (1995); Mars Kr from Pepin (1991); carbonaceous chondrite Kr from Krummenacher et al. (1962), Eugster et al. (1967), and Marti (1967), all re-normalized to Basford et al.’s air composition.



Nonradiogenic Xe isotopes in the atmosphere. The isotopic compositions of Xe components in the solar system have been more difficult to unravel. There is no suitable widespread solar system Xe component to use as a reference composition (see Ott 2002, this volume). The light isotopes of atmospheric Xe are related to both bulk chondritic and solar Xe by fractionation of $\sim 4.2\%$ per amu (first noted by Krummenacher et al. 1962), with a clear radiogenic excess of $\sim 7\%$ in ^{129}Xe from decay of ^{129}I . However, these components cannot be precisely related to the composition of the heavy Xe isotopes in

the atmosphere directly or by simple processes (such as mass fractionation) and addition of expected fissionogenic components. This holds using any common fractionation function (e.g., Fick's law, hydrodynamic escape), and so these compositions cannot serve as the primordial terrestrial composition (see Pepin 2000). This is shown in Figure 7, where unfractionated SW-Xe isotope ratios are plotted in Figure 7a and its fractionated residue in Figure 7b, both normalized to corresponding ratios in the present atmosphere. It is evident that when solar Xe is fractionated to match the light isotopes of the atmosphere, the $^{136}\text{Xe}/^{130}\text{Xe}$ ratio is well above atmospheric. Therefore fractionated SW-Xe contributes more ^{136}Xe relative to ^{130}Xe than the atmosphere actually contains. Subtraction of a fission component from air-Xe worsens the discrepancy. Consequently SW-Xe is ruled out as the primordial terrestrial composition. This exclusion clearly applies with even greater force to the meteoritic AVCC-Xe and Xe-Q compositions, since both are considerably richer in the heavy isotopes than SW-Xe (Table 1; Ott 2002).

Table 1. Isotopic compositions of solar-system xenon components discussed in this chapter.

Component	^{124}Xe	^{126}Xe	^{128}Xe	^{129}Xe	^{130}Xe	^{131}Xe	^{132}Xe	^{134}Xe	^{136}Xe
Air-Xe (a)	2.337(07)	2.180(11)	47.15(05)	649.6(06)	≡ 100	521.3(06)	660.7(05)	256.3(04)	217.6(02)
U-Xe (b)	2.928(10)	2.534(13)	50.83(06)	628.6(06)	≡ 100	499.6(06)	604.7(06)	212.6(04)	165.7(03)
NEA-Xe (c)	2.337(07)	2.180(11)	47.15(05)	605.3(29)	≡ 100	518.7(07)	651.8(13)	247.0(13)	207.5(13)
AVCC-Xe (d)	2.851(51)	2.512(40)	50.73(38)	653.3 (d)	≡ 100	504.3(28)	615.0(27)	235.9(13)	198.8(12)
Xe-Q (e)	2.810(13)	2.506(12)	50.77(16)	643.6(17)	≡ 100	505.6(11)	617.7(11)	233.5(08)	195.4(06)
SW ₁ -Xe (f)	2.939(70)	2.549(82)	51.02(54)	627.3(42)	≡ 100	498.0(17)	602.0(33)	220.7(09)	179.7(06)
SW ₂ -Xe (g)	2.928(10)	2.534(13)	50.83(06)	628.6(06)	≡ 100	499.6(06)	604.7(06)	220.7(09)	179.7(06)
Mars-Xe (h)	2.46(13)	2.14(13)	47.63(65)	1555(16)	≡ 100	513.9(35)	648.1(38)	259.7(18)	227.7(16)
Mars-Xe (i)	2.30(26)	≡ 2.10	47.3(14)	1556(08)	≡ 100	518.0(34)	652.9(42)	258.5(22)	226.9(16)

All isotope ratios are referenced to $^{130}\text{Xe} = 100$. Uncertainties ($\pm 1 \sigma$) in the last two digits of the listed relative isotopic abundances are indicated in parentheses.

(a) Terrestrial atmospheric Xe (Basford et al. 1973).

(b) Pepin (2000).

(c) Nonradiogenic Earth Atmosphere Xe (Pepin 1991).

(d) Average Carbonaceous Chondrite Xe (Pepin 1991). The listed value for ^{129}Xe is an average for CI and CM carbonaceous chondrites; the approximate range is from 636 to 671 (Mazor et al. 1970).

(e) Busemann et al. (2000).

(f) Measured SW values in acid-etching experiments on lunar ilmenites (Wieler and Baur 1994; Pepin et al. 1995).

(g) Adopted SW values: assumes that the SW-Xe composition is identical to U-Xe from ^{124}Xe through ^{132}Xe , with ^{134}Xe and ^{136}Xe equal to Wieler and Baur's (1994) SW ^{131}Xe -Xe measured values.

(h) Swindle and Jones (1997).

(i) Mathew et al. (1998).

A suitable initial composition for the atmosphere has been deduced from meteorites. Multi-dimensional isotopic correlations of chondrite data have been used to constrain a range of compositions that, when mass-fractionated, yields the light-isotope ratios of terrestrial Xe. In order to match the terrestrial heavy Xe isotope ratios, addition of radiogenic ^{129}I and a heavy Xe isotope component is required. Constraining the composition of the heavy isotope component to known fission spectra then defines the "U-Xe" composition and identifies ^{244}Pu -derived fissionogenic Xe as the heavy isotope component (see "Primordial Xe" section). This is compatible with meteorite data that indicates that the amount of ^{244}Pu present in the early solar system (Hudson et al. 1989) will produce SW Xe that will dominate over the production by ^{238}U (see Porcelli and Ballentine 2002) and be the correctly identified parent of fissionogenic Xe. Therefore,

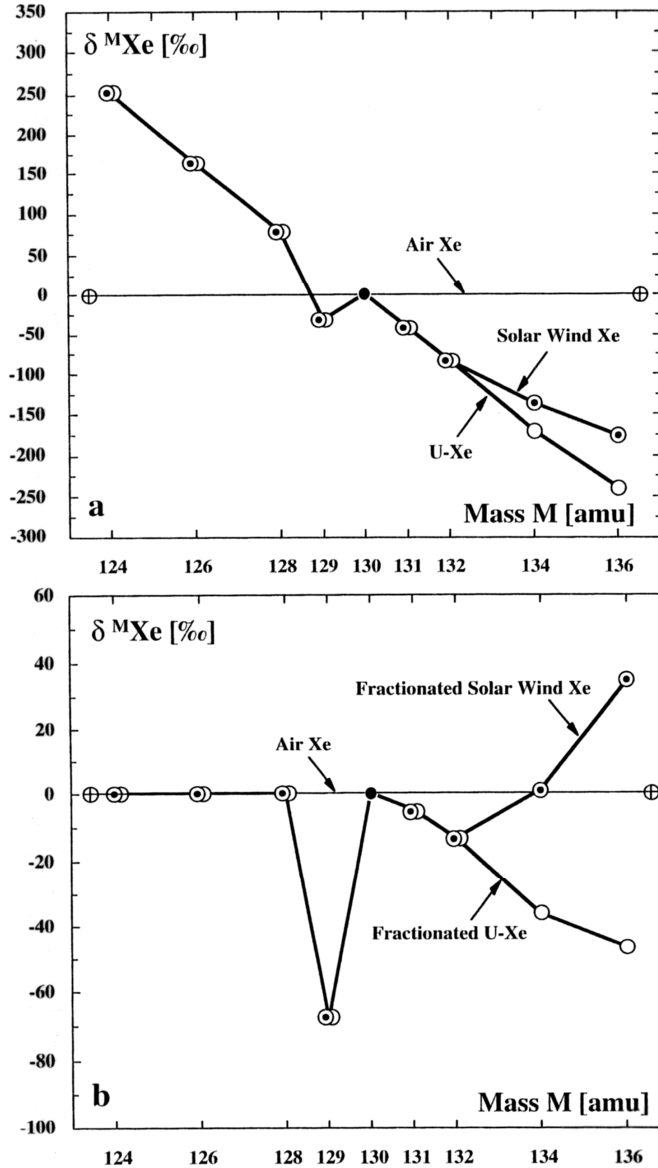


Figure 7. (a) Relationships of un-fractionated SW₂-Xe and U-Xe to terrestrial atmospheric Xe, plotted as permil differences from the ^MXe/¹³⁰Xe ratios in terrestrial air (Table 1). (b) As in Figure 6a, but now after hydrodynamic escape fractionation of SW₂-Xe and U-Xe to the extent required to match their ¹²⁴⁻¹²⁸Xe/¹³⁰Xe ratios to the corresponding Air-Xe values. Fractionated SW-¹³⁶Xe/¹³⁰Xe is elevated above the air ratio by ~10 times the 1 σ uncertainty in the SW ratio measurement.

fractionation of U-Xe, followed by addition of radiogenic ¹²⁹Xe and fissionogenic Xe, can produce the Xe atmospheric composition. The fact that U-Xe is underabundant in the heaviest isotopes compared to solar wind Xe (Fig. 7, “Primordial Xe” section) suggests that there is a heavy isotope component in the sun but not in the early Earth. This is puzzling, since solar wind Xe, presumably reflecting the Xe composition in the accretion disk, would arguably be the more plausible contributor to primordial planetary inventories. However, due to the relationship between solar Xe and the atmosphere (Fig. 7), such a problematic relationship will be evident in any composition for the Earth. Note that Igarashi (1995) obtained an alternative composition for atmospheric nonradiogenic Xe. However, this composition implies that the atmosphere contains in addition a heavy isotope component that has relative proportions of Xe isotopes that do not match the spectrum of either ²⁴⁴Pu or ²³⁸U, and so cannot be used to determine the fissionogenic Xe abundance of the atmosphere. While Igarashi (1995) suggested that this heavy component matched fractionated U-derived Xe, mass balance constraints make a terrestrial source for this implausible (Ballentine and Burnard 2002, this volume). Also note that the substantially different U-Xe and fission Xe compositions obtained by

Igarashi (1995) appear to reflect the use of a meteoritic database consisting largely of measurements on chemically separated phases that do not preserve mass balance (see Pepin 2000).

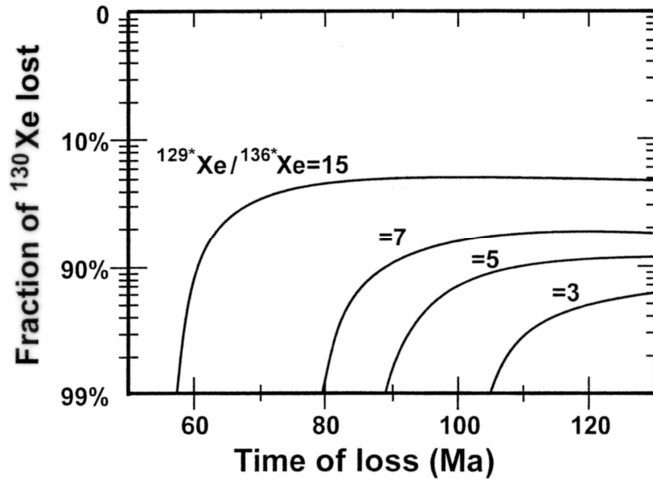
Nonradiogenic Xe isotopes in the mantle. The measured ratios of the nonradiogenic isotopes in MORB are indistinguishable from those of the atmosphere. However, some CO₂ well gases with presumably mantle-derived Xe have higher ¹²⁴⁻¹²⁸Xe/¹³⁰Xe ratios (Phinney et al. 1978; Caffee et al. 1999) that can be explained either by a mixture of ~10% solar or U-Xe and ~90% atmospheric Xe, or a mantle component that has not been fractionated relative to solar Xe to the same extent as atmospheric Xe. Due to the lower precision of MORB data and the pervasiveness of atmospheric contamination in MORB samples, it has not been possible to confirm that this feature is present throughout the upper mantle.

Atmospheric Xe closure ages. The fractionated U-Xe ratios of ¹²⁹Xe/¹³⁰Xe = 6.053 and ¹³⁶Xe/¹³⁰Xe = 2.075 are the present best estimates of the isotopic composition of nonradiogenic terrestrial Xe. Therefore, 6.8±0.3% of atmospheric ¹²⁹Xe (^{129*}Xe_{atm} = 1.7 × 10³⁵ atoms) and 4.65±0.50% of atmospheric ¹³⁶Xe (^{136*}Xe_{atm} = 3.81 × 10³⁴ atoms) are radiogenic. The ^{129*}Xe_{atm} is only 0.8% of the total ¹²⁹Xe produced since 4.57 Ga; such a low value cannot be accounted for by incomplete degassing of the mantle nor from any uncertainties in the estimated amount of ^{129*}Xe, and requires losses to space. Xe losses from the Earth to space must have occurred during early Earth history, when such heavy species could have been lost either from protoplanetary materials or from the growing Earth. Full accretion of the Earth may have occurred over ~100 Ma (Wetherill 1975). Over this time, almost all of the ¹²⁹I, and some of the ²⁴⁴Pu, had decayed to daughter Xe isotopes that could have been lost to space. A ‘closure age’ of the Earth could be calculated by assuming that essentially complete loss of radiogenic and fissionogenic Xe occurred until closure time t, followed by no further loss. In this case (Wetherill 1975; Pepin and Phinney 1976), the relative proportions of radiogenic ¹²⁹Xe and fissionogenic ¹³⁶Xe in the atmosphere can be used to obtain a closure age of 80 Ma (see discussion in Porcelli and Ballentine 2002, this volume). The implication is that losses occurred over an extended period as the Earth accreted. If atmospheric Xe loss occurred during a massive Moon-forming impact, then the closure period corresponds to the time after an instantaneous catastrophic loss event. A more complicated loss history will result in some revision in the closure time, but this is unlikely to be significant. Note that if Pu-derived ¹³⁶Xe was lost over about one half-life (80 Ma) of ²⁴⁴Pu, then ~40% of that produced subsequently in the Earth is in the atmosphere. This is compatible with the ⁴⁰Ar budget (see Porcelli and Ballentine 2002) and provides further support for the chosen nonradiogenic atmosphere composition.

Loss of nonradiogenic Xe from the atmosphere. None of the closure age calculations explicitly consider how nonradiogenic nuclides are retained. If the Earth had completely lost all Xe during the first ~100 Ma, there would be no nonradiogenic Xe present today. The nonradiogenic Xe budget can be examined with a simple two-stage model for the deep mantle reservoir. The reservoir begins with initial concentrations ¹C_{P0} and bulk silicate Earth parent element concentrations. At first, the reservoir behaves as a closed system, retaining all radiogenic ^{129*}Xe and fissionogenic ^{136*}PuXe. At some time t, all Xe isotopes are instantaneously depleted, leaving only a fraction f. This is followed by complete retention to the present day. Then (Porcelli et al. 2001)

$$\begin{aligned}
 &^{130}\text{Xe}_{\text{Atm}} = ^{130}\text{Xe}_{\text{Atm}_0} f \\
 \text{and} \quad &\frac{^{129*}\text{Xe}}{^{136*}\text{PuXe}} = \frac{^{129}\text{I}_0 [f + (1-f)e^{-\lambda_{129}t}]}{^{244}\text{Pu}_0 ^{136}\text{Y}_{244} [f + (1-f)e^{-\lambda_{244}t}]} \quad (1)
 \end{aligned}$$

Figure 8. The relationship between the time at which an instantaneous loss of Xe occurred and the fraction of gas lost. While $^{129}\text{Xe}/^{136}\text{PuXe} = 4.4$ for the atmosphere, estimates for the deep mantle vary between 3.5 and 10 (Porcelli et al. 2001), and require that losses are late (>60 Myr) and substantial ($>97\%$) from throughout the planet.



where $^{136}\text{Y}_{244}$ is the fission yield of ^{136}Xe . Figure 8 shows the fraction f of retained ^{130}Xe , plotted as a function of the time of loss, for various present values of $^{129}\text{Xe}/^{136}\text{PuXe}$. It can be seen that for each value of $^{129}\text{Xe}/^{136}\text{PuXe}$, there is a minimum time of loss, which corresponds to very large depletions; late losses correspond to the maximum fraction of Xe retained. For the atmosphere, $^{129}\text{Xe}/^{136}\text{PuXe} = 4.4$, and so the minimum time of loss is 95 Ma, with losses $>99\%$. Therefore, the Earth or Earth-forming materials initially contained at least 10^2 times the ^{130}Xe presently seen in the atmosphere. Loss of Xe during

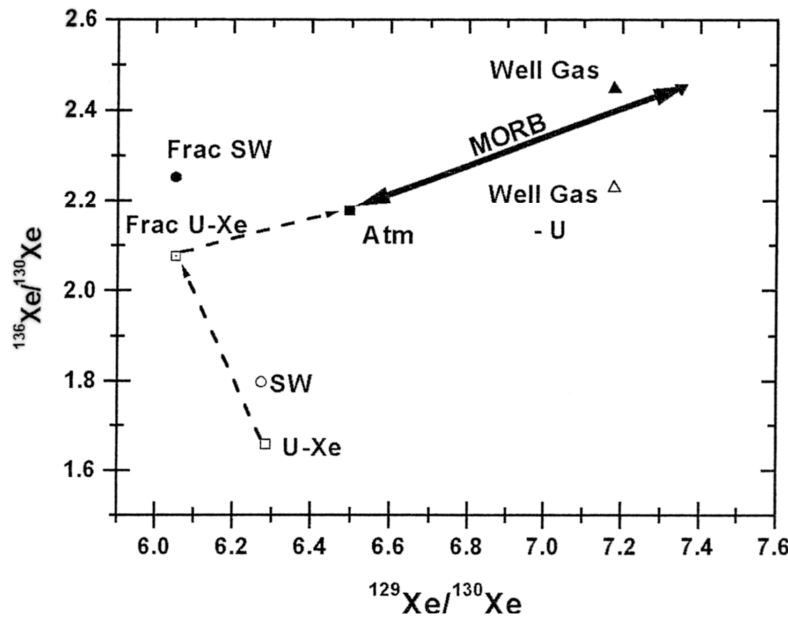


Figure 9. Xe isotope compositions of terrestrial precursors and present reservoirs. U-Xe, fractionated to match the light Xe isotopes (Fig. 7), provides an initial composition of the atmosphere, to which radiogenic ^{129}Xe and fissionogenic ^{136}Xe have been added. Similar fractionation of solar wind (SW) Xe produces Xe that is too heavy to supply the atmosphere. MORB typically have $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ ratios that are greater than the atmosphere due to radiogenic and fissionogenic additions and are correlated, with the range likely due to variable atmospheric contamination of samples. The most precise measurement of mantle Xe is for CO_2 well gas. When uraniumogenic Xe is subtracted, the well gas falls substantially below the MORB data, and indicating that the ratio of ^{244}Pu -derived ^{136}Xe to I-derived ^{129}Xe is lower than that of the atmosphere.

a single, brief event may have been driven by a Moon-forming impact. While more complicated loss histories can be constructed, the general conclusion that very large losses of Xe occurred is inescapable.

Radiogenic Xe in the mantle. Data for MORB indicate that the mantle has $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ ratios greater than those of the atmosphere (Fig. 9). There is considerable uncertainty and debate regarding how much of the ^{136}Xe excess is due to ^{244}Pu , rather than ^{238}U , decay. The most recent data suggest that ~30% is due to ^{244}Pu decay (Kunz et al. 1998), with considerable uncertainty due to scatter in the data. This is also consistent with measurements of mantle-derived Xe in well gases that indicate <20% is Pu-derived (Phinney et al. 1978; see further discussion in Porcelli and Ballentine 2002). It has been shown that these higher ratios cannot be due to early degassing of the mantle, but rather reflect the composition of a deep mantle reservoir that has evolved independently and where Xe produced by ^{129}I and ^{244}Pu is stored (Ozima et al. 1985; Porcelli and Ballentine 2002). This reservoir has been explicitly equated with a gas-rich source of high $^3\text{He}/^4\text{He}$ mantle (Porcelli and Wasserburg 1995a). While models for the distribution of noble gases within the mantle are still debated, the greatest obstacle to consensus has been how to maintain two separate mantle reservoirs (for MORB and OIB sources) throughout Earth history, and so it is more likely that the long-term storage of high $^3\text{He}/^4\text{He}$ ratios as well as high $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ occur in the same reservoir, rather than necessitating the maintenance of three mantle reservoirs.

Xe loss from the mantle. The $^{129}\text{Xe}/^{136}\text{PuXe}$ ratio of the mantle is not substantially different from that of the atmosphere, indicating that substantial losses also occurred from within the Earth. A value of $^{129}\text{Xe}/^{136}\text{PuXe} = 10$ can be obtained from MORB data, although with considerable uncertainty in the amount of Pu-derived Xe as discussed above. In this case, the minimum time of loss from the deep mantle is ~70 Ma and a maximum fraction retained is $f \sim 0.02$ (Fig. 8). Therefore, at least 98% of the Xe was lost. Although further refinements can be made for calculating these values by considering the possible amounts of subducted Xe that is in the mantle (Porcelli et al. 2001), the results are qualitatively the same. If the Xe now seen in the upper mantle has been stored since early Earth history in an undegassed reservoir along with the high OIB $^3\text{He}/^4\text{He}$ ratios, then this reservoir initially contained = 10^2 times more Xe, and so also He, than it has at present. Taking the calculated closed system ^3He concentration of $(6.1-7.9) \times 10^{10}$ atoms $^3\text{He}/\text{g}$, then = $\sim 7 \times 10^{12}$ atoms $^3\text{He}/\text{g}$ must have been initially trapped. Using $^3\text{He}/^{22}\text{Ne} = 7.7$, then at least 10^{12} atoms $^{22}\text{Ne}/\text{g}$ was trapped. This may be compared to the value obtained by dividing the atmospheric ^{22}Ne inventory into the mass of the Earth of 3×10^{10} atoms/g. The initial gas-rich state of the Earth appears to have involved all reservoirs.

Noble gases on Venus

There are limited probe data available for the isotopic composition of the Venus atmosphere, and of course none available for noble gases in the Venus interior. Wieler (2002, this volume, p. 41: his Table 8 and references therein) provides the most recent compilation and assessment of the available data.

Nonradiogenic noble gases. For Ne, both of the two $^{20}\text{Ne}/^{22}\text{Ne}$ ratios derived from different data bases (11.8 ± 0.6 and 12.15 ± 0.40 : see Wieler's (2002) Table 8) require some fractionation relative to the solar value, although not quite to the same extent as that of the terrestrial atmosphere. The constraint on the $^{21}\text{Ne}/^{22}\text{Ne}$ ratio of <0.067 cannot be used to further limit the source of Ne. The $^{36}\text{Ar}/^{38}\text{Ar}$ value of 5.45 ± 0.10 measured by Venera spacecraft instruments is nominally somewhat above the terrestrial ratio but is essentially indistinguishable from it within error.

Radiogenic nuclides. The measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is 1.11 ± 0.02 , substantially less radiogenic than the terrestrial atmosphere. For a mixing ratio of 21-48 ppm (Donahue and Pollack 1983), the atmosphere contains $(1.8\text{-}4.4) \times 10^{41}$ atoms ^{40}Ar . Divided by the mass of the planet, this corresponds to $(3.6\text{-}9.0) \times 10^{13}$ atoms $^{40}\text{Ar}/\text{g}$. This is 0.2-0.5 times the value for the Earth. However, Venus appears to be deficient in K. Data for the K/U ratio of the surface indicate that $\text{K}/\text{U} = 7220 \pm 1220$ (Kaula 1999), or 0.57 ± 0.10 times that of the value of 1.27×10^4 commonly taken for the Earth. Assuming that Venus has the same U concentration as the total Earth of 14 ppb, then 12-28% of the ^{40}Ar produced in Venus is now in the atmosphere. This indicates that a substantial inventory of ^{40}Ar remains within the planet, possibly also accompanied by up to an equivalent fraction of nonradiogenic noble gases. In contrast, at least 40% of terrestrial ^{40}Ar is in the atmosphere. The fraction of ^{40}Ar in the Venus atmosphere has been related to tectonic activity and heat loss on the planet (Sasaki and Tajika 1995; Turcotte and Schubert 1988; Kaula 1999).

Noble gases on Mars

While there are probe data for the atmosphere of Mars, high precision information has also been obtained from Martian meteorites. These have also provided some information about the interior source regions of Martian volcanics. The most recent review is by Swindle (2002, this volume).

Nonradiogenic noble gases. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of the Martian atmosphere is not well determined. The estimate of 10.1 ± 0.7 from SNC meteorite data (Pepin 1991) is within error of the terrestrial atmosphere, and thus substantially lower than the solar value. The $^{38}\text{Ar}/^{36}\text{Ar}$ ratio is highly fractionated relative to the solar Ar ratio of 0.17; SNC meteorite analyses yield values ranging from 0.24 ± 0.01 (Pepin 1991) to 0.26-0.30 (Bogard 1997; Garrison and Bogard 1998). The Kr isotopic composition of the atmosphere of Mars (Pepin 1991; Garrison and Bogard 1998) appears to be essentially indistinguishable from that of solar wind Kr, as seen in Figure 6, although it is possible that it is slightly fractionated to an isotopically somewhat lighter composition (see Garrison and Bogard 1998; Swindle 2002, this volume).

Primordial Xe (i.e., those isotopes unaffected by fissiogenic or radiogenic inputs) in the Martian atmosphere is greatly fractionated relative to the solar and chondrites compositions, with preferential enrichment of the heavy isotopes (Swindle et al. 1986; Mathew et al. 1998; Table 1). However, there are some uncertainties with constraining the precise composition of this Xe and this affects not only identification of the initial source of Martian Xe but also determination of the precise amounts of radiogenic and fissiogenic Xe in the atmosphere, particularly the latter (see "Primordial Xe" section and discussions below of radiogenic ^{129}Xe and fissiogenic ^{136}Xe budgets).

Radiogenic ^{40}Ar . The atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio has been measured by Viking to be 3000 ± 400 (Pepin and Carr 1992), although a lower value of ~ 1800 has been deduced from meteorite data (Pepin and Carr 1992; Bogard 1997; Bogard et al. 2001). Based on the Viking data, there are $(7.0 \pm 1.4) \times 10^{39}$ atoms ^{40}Ar in the atmosphere. The Mars mantle has been estimated to have 305 ppm K (Wänke and Dreibus 1988), so that 3.3×10^{41} atoms ^{40}Ar have been produced in Mars. Therefore, only 2% of Martian ^{40}Ar has degassed to the atmosphere, and most of the planet interior has retained the ^{40}Ar produced throughout its history. The history of degassing of ^{40}Ar from the interior has been discussed in several studies (Volkov and Frenkel 1993; Sasaki and Tajika 1995; Hutchins and Jakoski 1996; Tajika and Sasaki 1996).

The radiogenic ^{129}Xe budget. Martian atmospheric Xe clearly contains a considerable fraction of radiogenic ^{129}Xe . It has been estimated that the silicate portion of

Mars contains 32 ppb iodine (Wänke and Dreibus 1988). Assuming that $^{129}\text{I}/^{127}\text{I} = 1.1 \times 10^{-4}$ at 4.57 Ga (Hohenberg et al. 1967), then 8.44×10^{36} atoms ^{129}Xe have been produced in Mars or precursor materials. Using fractionated CI chondrite Xe or solar Xe for the nonradiogenic light Xe isotope composition (see discussion in “Primordial Xe”), the atmosphere is calculated to contain only 0.092% of what has been produced. Assuming there is none remaining in the planet, this corresponds to a closure age of 160 Ma. However, if only 2% has degassed (like ^{40}Ar) to the atmosphere, then a closure age of 70 Ma is obtained. This value is similar to that of the Earth, and suggests that there may also have been losses of volatiles from Mars over the same extended period of accretion.

The fissionogenic ^{136}Xe budget. The amount of ^{136}Xe produced in Mars or accreting materials, assuming that the silicate portion of Mars has 16 ppb of ^{238}U at present (Wänke and Dreibus 1988) and initially had $^{244}\text{Pu}/^{238}\text{U} = 0.0068$ (Hudson et al. 1989), is 1.9×10^{34} atoms ^{136}Xe from ^{244}Pu and 7.2×10^{32} atoms ^{136}Xe from ^{238}U . In contrast, there is a total of 2.8×10^{33} atoms ^{136}Xe in the atmosphere. Up to ~5% of the atmospheric ^{136}Xe may be Pu-derived (see “Primordial Xe” below); if so, and the closure age for Mars is 70 Ma, then 1-2% of the ^{244}Pu produced in the solid planet has degassed. This is consistent with the ^{129}Xe and ^{40}Ar budgets. As noted in the section *Primordial Xe*, plutogenic ^{136}Xe could comprise much less than 5% of the total atmospheric inventory, requiring even less planetary degassing and greater very early isolation of interior volatiles from the atmosphere. Reports of significant abundances of ^{244}Pu fission Xe in several SNC meteorites do in fact point strongly to its efficient retention in the Martian crust (Marty and Marti 2002; Mathew and Marti 2002). Further discussion of the abundances of daughter Xe isotopes in the atmosphere is provided by Swindle and Jones (1997). Musselwhite et al. (1991) and Musselwhite and Drake (2000) discuss the distribution of I and the degassing of radiogenic ^{129}Xe .

Martian interior gases. Martian meteorites contain components other than those derived directly from the atmosphere (see detailed discussion by Swindle 2002, this volume). While some appear to be derived from the atmosphere by secondary processes such as alteration, noble gases in the dunite meteorite Chassigny appear to represent a distinct interior reservoir. Information on the relative abundances of the heavier noble gases (Ott 1988) suggests that the $^{84}\text{Kr}/^{132}\text{Xe}$ ratio (1.2) is lower than both the Martian atmosphere (20) and solar (16.9) values, but is similar to that of CI chondrites. If this is truly a source feature, it indicates that heavy noble gases trapped within the planet suffered substantially different elemental fractionation than the atmosphere. The interior $^{84}\text{Kr}/^{36}\text{Ar}$ ratio of 0.06 is much higher than the solar value of 2.8×10^{-4} , but it is close to the atmospheric value of 0.02 and so does not display the same contrast as the Kr/Xe ratio. It is not possible at present to conclusively determine whether the measured elemental abundance ratios reflect an interior reservoir that was initially different from atmospheric noble gases, rather than due either to planetary processing or transport and incorporation into the samples.

The isotopic composition of the Martian interior is only available for Xe. The nonradiogenic isotope ratios found in Chassigny (a dunite that is possibly mantle-derived) appear to be indistinguishable from solar values (Ott 1988; Mathew and Marti 2001), and so do not exhibit the strong fractionation seen in the atmosphere. The relative abundances of ^{129}Xe and ^{136}Xe are also close to solar, and so there is little scope for radiogenic additions, indicating that this reservoir had a high Xe/Pu ratio, at least during the lifetime of ^{244}Pu . In contrast, this solar Xe appears to be accompanied by a Kr/Xe ratio that is fractionated with respect to the solar value. Data from other meteorites indicate that there are other interior Martian reservoirs that contain solar Xe but with

resolvable fissiogenic contributions (e.g., Nakhla: Mathew and Marti 2002), and so have had lower Xe/Pu ratios. Therefore the interior appears to be relatively undegassed, with high ratios of primordial Xe to parent elements.

ACQUISITION OF PLANETARY NOBLE GASES

The key diagnostic volatiles for tracing atmospheric origin and nonbiogenic evolution are the noble gases, nitrogen as N₂, and carbon as CO₂. Signatures of origin would be expected to survive most clearly in the chemically inert noble gases. Their record is complex, however, and not readily interpreted. As discussed in the preceding sections, absolute abundances of noble gases in the atmospheres of Earth, Venus and Mars and in the carbonaceous chondrites display highly variable depletions with respect to solar abundances, and isotopic patterns in each of these volatile reservoirs are generally distinct from each other and from inferred compositions in the sun and primitive solar nebula. Models of origin based on seemingly straightforward clues in one subset of this extensive data base have historically encountered inconsistencies in another. A celebrated example of this kind of difficulty involves neon-argon distributions. Measured ²⁰Ne/³⁶Ar elemental ratios are roughly the same, within a factor two or so, on Earth, Venus, and Mars, and in bulk samples of the primitive CI carbonaceous chondrites. This approximate concordance has prompted much discussion in the modeling literature (see, for example, the review by Donahue and Pollack 1983), usually with the view that it implies accretion of common parental material as the source of at least these two gases in inner solar system bodies. Isotope systematics, however, argue against this interpretation since the required isotopic uniformity is absent: ²⁰Ne/²²Ne on Venus is higher and ³⁶Ar/³⁸Ar on Mars much lower than the corresponding ratios on the Earth and in CI meteorites (Pepin 1991; Pepin and Carr 1992).

Prior to the mid-1980s, most attempts to account for the origin of terrestrial planet atmospheres focused, as in the example above, on deriving the elemental abundance patterns of atmospheric noble gases from primordial meteoritic or nebular reservoirs. One common approach, termed “gas-poor” models by Donahue and Pollack (1983), was to regard an atmosphere as a mixture of gases acquired by accretion on an initially volatile-poor planet of a veneer of known (or occasionally hypothetical) volatile-rich meteoritic or cometary materials or carriers of adsorbed nebular gases. Another class of “gas-rich” models postulated the initial presence and subsequent dissipation of gravitationally captured or impact-degassed primordial atmospheres on the planets themselves. With a few exceptions, comparatively little attention was paid to isotopic distributions, in particular those of the heavy species krypton and xenon, or to astrophysical environments in which evolutionary processing might plausibly have occurred.

The successes and problems of many of these “gas-poor” and “gas-rich” models are discussed by Donahue and Pollack (1983). A point to be emphasized here is that the gas-poor theories are intrinsically unable to account for the range of isotopic variability seen in planetary atmospheres. The processes of sorption and mixing invoked in these models do not fractionate isotopes (although mixing of isotopically different components can certainly generate variable compositions), yet there is strong evidence that such fractionating mechanisms have been at work. For this reason, gas-rich theories that assume the presence of primordial atmospheres of whatever origin on growing or fully accreted planetary bodies, or on (or in) large preplanetary planetesimals, appear fundamentally more attractive. They offer the potential for isotopic fractionation in the process(es) that subsequently dissipated these atmospheres, and the possibility that the variable distributions of noble gas abundances and isotopes seen in present-day planetary atmospheres may be understood as reflecting different degrees of processing on the individual bodies.

Early post-nebular solar wind

Noble gases implanted by low-energy solar wind irradiation are typically retained in solar-like elemental abundance proportions in lunar and meteoritic dust grains, particularly the three heaviest species. Implantation typically extends into the upper few tens of nanometers of the irradiated materials, and so the amounts of noble gases that can be accumulated in this way depend upon their surface areas. The irradiation of dust in the solar nebula will clearly contribute the highest concentrations of noble gases to the subsequently accumulated planetary bodies. An available analog is the fine material found in the lunar regolith. Accretion of planetesimals containing ~25-40 wt % of solar-wind-implanted dust (an enormous fraction, probably attainable only in small objects with thick regoliths of irradiated dust grains) loaded to lunar regolith levels in Xe, Kr and Ar but depleted ~100-fold in ^{20}Ne , could account for the absolute noble gas abundances in Venus's atmosphere. Neon (and helium) can be preferentially lost from irradiated grains by subsequent heating, or depleted even at comparatively low temperatures by rapid diffusion from certain mineral structures, notably plagioclase (e.g., Frick et al. 1988). However, the presence of substantial dust in the nebular disk prior to aggregation also greatly dampens penetration of solar wind out to much of the planet-forming region, while clearance of this dust results in larger targets and therefore smaller fractions by weight of irradiated material.

This general kind of solar wind source for noble gases on the terrestrial planets has been proposed in various contexts by Wetherill (1981), Donahue et al (1981), and McElroy and Prather (1981). Wetherill's (1981) model provides the large ^{36}Ar abundance on Venus by accretion of material irradiated in the inner edge of the nebular disk. He perceived the major difficulty of the model to be that of confining accretion of solar-wind-rich materials largely to just this planet, given the likelihood that gravitational scattering would tend to disperse it throughout the inner solar system. But it is important to note that this may no longer be a fatal objection. As described later in the *Hydrodynamic escape* section, Earth could have acquired a compositionally Venus-like primary atmosphere as well, later fractionated by partial loss, and there is evidence that solar-composition noble gases may have dominated the primordial atmosphere on Mars. The principal problem now with this hypothesis is that Xe in the atmospheres of the early Earth and Mars appears to have differed in isotopic composition—SW-Xe or CI-Xe on Mars, but U-Xe on Earth (see *Primordial Xe* below). Nevertheless the possibility that a solar-wind source of this kind contributed to some degree to noble gas inventories in the interiors or primordial atmospheres of the terrestrial planets should be taken seriously. It could turn out on compositional grounds to be more plausible than either the gravitational capture or icy planetesimal sources discussed below. Moreover Sasaki's (1991) arguments for off-disk penetration of an early and intense solar wind flux into a post-nebular environment rich in fine collisional dust may imply the existence of an ancient reservoir of abundant and heavily loaded carriers of solar-like noble gases. Such a source has been considered for providing the noble gases presently found within the Earth's mantle. Podosek et al. (2000) argued that the present concentrations of Ne estimated for a deep mantle gas-rich reservoir could have been derived from irradiated, km-sized planetesimals (assuming that sufficient turnover of the surfaces occurred so the process was not limited by grain saturation effects). This process would not have been limited by self-shielding by solid material across the accretionary disk due to removal of dust into larger bodies, and thus requires that a substantial fraction of the present mass of the Earth remained as small dispersed planetesimals until after nebula gas had cleared. Also, the gases must be retained in growing planetesimals and ultimately into the growing Earth, without being lost due to impacts or melting. This model cannot be assessed further without greater understanding of the chronology of accretion and gas dispersal, but it

remains as a possible explanation for the origin of noble gases within the mantle. It should be noted that a definitive identification of trapped primordial Ne in the mantle as Ne-B (see *Solar Ne within the Earth* section) would provide strong support for this mechanism.

Adsorption on pre-planetary grains or protoplanetary bodies

Laboratory studies have shown that noble gases exposed to particular kinds of finely divided solid materials are adsorbed on or within the surfaces of individual grains. Adsorption is most efficient for various forms of carbon, where it appears to reflect intrinsic structural properties (Frick et al. 1979; Niemeyer and Marti, 1981; Wacker et al. 1985; Zadnik et al. 1985; Wacker, 1989), but has also been experimentally demonstrated for other minerals (Yang et al. 1982; Yang and Anders 1982a,b) and for polymineralic meteorite powder (Fanale and Cannon 1972). Moreover the process occurs naturally in sedimentary materials (Canalas et al. 1968; Fanale and Cannon 1971; Phinney 1972; Podosek et al. 1980, 1981; Bernatowicz et al. 1984). Adsorbed gases on these substrates generally display fractionation patterns, relative to ambient gas-phase abundances, in which heavier elements are enriched. For the most part these elemental fractionations are remarkably uniform, considering the wide range of experimental and natural conditions under which they are produced. Although occasional isotopic effects have been reported in natural samples (Phinney 1972), they are not observed in equilibrium adsorption in the laboratory (Bernatowicz and Podosek 1986).

The decline in solar-normalized noble gas abundance ratios from Kr to Ne in planetary atmospheres and meteorites is qualitatively similar to many of the adsorption fractionation patterns seen in the laboratory and in terrestrial sedimentary rocks, as shown in Figure 2. This has led to a suspicion that adsorption of nebular gases on meteoritic and protoplanetary materials has played a role in establishing these ratios. Adsorption of isotopically solar noble gases, however, cannot by itself generate the fractionated isotopic patterns seen in planets, and laboratory estimates of single-stage gas/solid partition coefficients are too low to account for planetary noble gas abundances by adsorption on free-floating nebular dust grains. Nevertheless adsorption or solution from a gas phase could well have been an important mechanism for supplying primordial volatiles to planets, if it occurred from a reservoir well above nebular pressures—for example, as discussed in the following section, by gravitational capture of atmospheres on protoplanetary or planetary bodies that had grown to the critical size for the process to be effective.

Gravitational capture

Capture by growing planets. A potentially powerful noble gas source for the terrestrial planets is direct capture of co-accreting primordial atmospheres from the nebula during planetary growth. Substantial gravitational capture of ambient gases requires the growth of protoplanets to appreciable masses (at least to ~Mercury-Mars size) prior to dissipation of the nebular gas phase. The extent to which this would have occurred hinges on the relative timing of nebular dissipation versus planetary accretion. Current estimates of timescales for loss of circumstellar dust and gas, from observation and theory, are on the order of ~10 Ma or perhaps somewhat less (Podosek and Cassen 1994), much shorter than the ~100 Ma or more for planetary growth to full mass in the standard model of planetary accumulation (Wetherill 1986, 1990a). Nebular lifetimes inferred from astronomical observation, however, are based solely on evolution of their fine dust component. Measurements of molecular line emissions that could at least set upper limits on the longevity of the gas-phase component in “naked” T-Tauri disks are challenging, and data are sparse (Strom et al. 1993). There is no reason to believe that disappearance of micrometer-size dust from infrared detectability, say by accretion into

larger grains, would necessarily be coincident with gas loss. According to the standard model, terrestrial planet growth to roughly 80% of final masses occurred within ~20 Ma (Wetherill 1986). So if the observed dust clearing signals the beginning of planet-building, and a significant remnant of gas survived in the inner solar accretion disk for another 10-20 Ma or so, substantial gravitational capture would have taken place, at least on proto-Earth and proto-Venus.

It would appear that current observations and modeling cannot rule firmly for or against gravitational capture of massive solar-composition primary atmospheres on Earth and Venus. The extent to which this occurred, creating tenuous or dense, massive atmospheres, depends upon the mass of the protoplanets at the time of nebular gas dispersal. If it did occur, subsequent evolution from primary to present-day noble gas inventories and compositions must have involved loss processes that fractionated both elements and isotopes to generate the presently observed compositions (Fig. 2). There is presently no reason to assume elemental fractionation in the capture process itself, although it may be that this possibility needs more theoretical study.

Capture by planetary embryos. While the atmospheres captured by these small bodies may not provide sufficient terrestrial noble gas abundances in themselves, sufficient quantities of gases may have accumulated within the protoplanetary bodies by gas adsorption on surface materials followed by burial below the surface during continuing accretion (Pepin 1991). The process may have played an important role in creating internal volatile reservoirs for later outgassing of secondary atmospheres on the terrestrial planets, especially for the heavy noble gases. Protoplanetary cores, growing through sizes of a few lunar masses in the presence of nebular gas at temperatures and pressures estimated from astronomical observations and from accretion disk models, would have gravitationally captured atmospheres that may have then been incorporated into the solid body. Interaction of the gases with the surface is governed by the pressure at the base of the atmosphere, which depends on the thermal structure of the atmosphere. This in turn is a sensitive function of atmospheric opacity, which is difficult to estimate, although amplifications of surface pressure by ~4-6 orders of magnitude above that of the ambient nebula are likely (Pepin 1991). Adsorption and occlusion of these surface gases on and within growing planetary embryos would appear to be a natural consequence of their accumulation, in the presence of nebular gas, to bodies of up to ~Mercury-size within <1 Ma (Wetherill 1990b; Wetherill and Stewart 1993).

Another consideration bearing on the probable volatile-rich nature of planetary embryos is that impact velocities of materials accreting to form these small bodies are generally too low to promote efficient degassing of the impactors themselves. Consequently their volatiles also tend to be buried within the growing embryos (Tyburczy et al. 1986). If noble gases were acquired by these mechanisms, atmospheric formation would then occur by subsequent degassing and isotopic fractionation during loss to space. Noble gases trapped within the Earth and incorporated into the present deep mantle would exhibit solar isotopic compositions but elemental fractionation; for example, adsorption in laboratory experiments strongly fractionates ambient Ne and Ar (in favor of Ar) by factors of ~10 to >50.

Evidence of such a deep Earth abundance pattern coupled with solar isotopic compositions would be a strong indicator that adsorption could have played a role early in the Earth's accretional history (Pepin 1991, 1998). Although there is evidence that solar-like light noble gas isotopic compositions exist, the abundance pattern of trapped noble gases in the Earth cannot be easily constrained, since there is the possibility that subduction of heavy noble gases has since altered the pattern. With a Mars-size terrestrial embryo and the high value of 2×10^{-5} for the Ne Henry's constant assumed in Pepin's

(1991) treatment of adsorption, the amount of adsorbed Ne that could presently be stored in a gas-rich lower mantle may be achieved. However it is too low to account for an initial deep Earth abundance of 10^{12} atoms $^{22}\text{Ne}/\text{g}$ (see “Xe loss from the mantle” above). This suggests that if adsorption had been responsible for providing the heavier noble gases, another process, such as dissolution into surface magma, would be required to increase the ^{20}Ne inventory above the level supplied by adsorption.

Gravitational capture and dissolution into molten planets. If the Earth reached sufficient size in the presence of the solar nebula, a massive atmosphere of solar gases would have been gravitationally captured and supported by the luminosity provided by the growing Earth, and the underlying planet would have melted by accretional energy and the blanketing effect of the atmosphere (Hayashi et al. 1979). Gases from this atmosphere would have been sequestered within the molten Earth by dissolution at the surface and downward mixing (Mizuno et al. 1980). This mechanism can provide solar noble gases into the deep Earth with relative elemental abundances that have been fractionated according to differences in Henry’s constants for solubility in silicates (with depletion of heavy noble gases). Initial calculations found that at least an order of magnitude more Ne than presently found in the deep mantle could be dissolved into the Earth unless the atmosphere began to escape when the Earth was only partially assembled (Mizuno et al. 1980; Mizuno and Wetherill 1984; Sasaki and Nakazawa 1990; Sasaki 1999). As noted above, the present abundances may be 10^{-2} times that of initial concentrations, and Porcelli et al. (2001) and Woolum et al. (1999) considered the conditions required to dissolve sufficient Ne to account for the initial deep mantle inventory prior to losses at $\sim 10^8$ a. If it is assumed that equilibration of the atmosphere with a thoroughly molten mantle was rapid, and uniform concentrations were maintained throughout the mantle by vigorous convection, then the initial abundances of gases retained in any mantle layer reflect surface noble gas partial pressures when that layer solidified. The depth at which solidification occurs is determined by the surface temperature and the efficiency of convection in the molten mantle. Therefore, initial distributions of retained noble gases would be determined by the history of surface pressure and temperature during mantle cooling and solidification, i.e., the coupled cooling of Earth and atmosphere. For typical solubility coefficients (e.g., Lux 1987; Carroll and Stolper 1993; Shibata et al. 1998), a total surface pressure of the order of 100 atm under an atmosphere of solar composition was required to establish the initial deep mantle Ne concentration (Porcelli et al. 2001), along with surface temperatures high enough to melt the deep mantle (~ 4000 K). Therefore, for this model of the origin of deep He and Ne to be viable, two conditions must be shown to be achievable: (1) the surface pressures necessary to dissolve the required abundances of noble gases are achieved, and (2) the surface temperatures sufficient to melt to lower mantle depths are reached. The dense atmosphere is a balance between the gravitational attraction of the nebula-derived gases and expansion due to the Earth’s luminosity (energy released by accreting planetesimals and the cooling Earth). The nebular temperature and pressure provide boundary conditions, and the atmospheric opacity (which controls the rate of energy loss to space) is a critical parameter. High luminosities (or low opacities) increase the surface temperature but lower the pressure, while decreasing nebular pressures will generate lower surface pressures and temperatures. Therefore, the temperature and pressure at the base of the atmosphere evolved as the energy released by accretion declined with time once planet assembly approached completion, and as the nebular pressure declined during nebula dispersal. Woolum et al. (1999) demonstrated that the necessary conditions were met under a range of parameter values for both convective and radiative atmospheric structures. However, the complexities in determining the effects of the composition of the lower atmosphere (which was probably strongly contaminated by

evaporated terrestrial material that would have had a marked effect on opacity) and the transition from optically thick to thin atmospheric conditions presently remain to be resolved.

It should be noted that not all situations facilitate the dissolution of atmospheric gases. At low nebular pressures and high initial luminosities, it is possible that the initial cooling phases occurred when the entire atmosphere was optically thin; in some such cases, rapid magma solidification occurs without the incorporation of significant concentrations of atmospheric gases. However, in the presence of a massive atmosphere that promotes gas dissolution, the mantle cooling time is greatly extended over that which would otherwise occur (Tonks and Melosh 1990). Solidification times then commonly exceed a million years, allowing substantial time for downward convection of noble gases. Overall, it appears that sufficient He and Ne (along with associated Ar, Kr, and Xe) can be incorporated into the Earth over a wide range of conditions by this mechanism.

As discussed above, the plausibility of this gravitational capture mechanism depends upon whether a sufficient mass of the Earth accretes prior to dispersal of nebular gases, and further work is required to determine if dispersal of the nebula can extend over such time periods.

Accretion of volatile-rich planetesimals

Comet accretion models. Noble gases, as well as water, carbon, and nitrogen, could have been supplied to the inner planets by accretion of volatile-rich icy comets scattered inward from the outer solar system. Although noble gas isotopic distributions in comets are unknown, solar isotopic compositions would be expected in cometary gases acquired from the nebula. There is experimental evidence that the relative elemental abundances of heavier species (Xe, Kr, and Ar) trapped in water ice at plausible comet formation temperatures (~30 K) approximately reflect those of the ambient gas phase, and trapped noble gas abundances per gram of water are substantial (Bar-Nun et al. 1985; Owen et al. 1991). The compositional characteristics of an icy planetesimal source in comet accretion models for Venus, discussed below, require occlusion of nebular noble gases with approximately unfractionated elemental ratios for Ar:Kr:Xe but much lower Ne. Thermodynamic modeling suggests that noble gases incorporated in clathrates do indeed have low Ne/Ar ratios, but do not reflect ambient gas-phase compositions for Xe/Ar and Kr/Ar and instead are strongly enriched in the heavier species (Lunine and Stevenson 1985). Clathrated gases therefore appear unlikely to be the source of atmospheric noble gases, at least for Venus, and one must appeal to physical adsorption on ice.

Incorporation of a few percent or less by mass of icy cometary matter into an accreting terrestrial planet could potentially have supplied heavy noble gases of solar composition to its primary atmosphere, in addition to enough hydrogen (as H₂O) to fuel the subsequent hydrodynamic escape episode that generated the observed isotopic fractionations (see below). This kind of source is particularly attractive in that the low Ne/Ar ratio expected for trapping of ambient gases in amorphous ice at temperatures >20-25 K (Owen et al. 1991; Owen and Bar-Nun, 1995ab) would provide a natural explanation for the underabundance of Ne in the otherwise solar-like Venus pattern (Figs. 2 and 12). A cometary carrier of primordial Venus volatiles with just these characteristics has been proposed (Owen 1987, Hunten et al. 1988, Owen et al. 1991; Owen and Bar-Nun 1995a,b).

At likely nebular temperatures and pressures at its radial distance, Mars is too small to have condensed a dense early atmosphere from the nebula even in the limiting case of isothermal capture (Hunten 1979; Pepin 1991). Therefore, regardless of the plausibility of gravitational capture as a noble gas source for primary atmospheres on Venus and

Earth, some other way is needed to supply Mars. An early inward flux of icy planetesimals would have contributed to all three of the terrestrial planets, even if it dominated the noble gas budget only on Mars. Accretion of a substantial mass of volatile-rich bodies resembling the present-day carbonaceous chondrites may be another possibility. Swindle et al. (1986) pointed out that the isotopic composition of Martian atmospheric Xe calculated from their SNC meteorite measurements was compatible with that of mass-fractionated CI-Xe, consistent with Dreibus and Wänke's (1985, 1987, 1989) SNC-based geochemical model of Mars' bulk composition which calls for a ~40% mass fraction of volatile-rich, oxidized CI-like material in the planet. However subsequent expansion and recalculation of Xe data from the SNC meteorites now suggest that solar-wind Xe is a viable alternative to CI-Xe as the principal atmospheric constituent on early Mars (see "Primordial Xenon" section below), raising the challenging question of how Mars could have acquired a large solar Xe component while Earth apparently did not.

A number of arguments can be made in favor of cometary carriers for inner planet volatiles. As noted above, reduction of the Ne/Ar ratio relative to the solar ratio, resembling the elemental pattern on Venus, is likely in such ices. Modeling discussed below indicates that a source of this nature could have supplied essentially identical primary atmospheres to both Venus and Earth if an initially Venus-like atmosphere on Earth were later elementally fractionated in hydrodynamic escape powered by a giant Moon-forming impact.

Accretion of icy cometary matter has been widely viewed as a plausible source for Earth's water. The D/H ratio in seawater, however, is substantially lower—by a factor of ~2—than in the few comets where D/H has been measured (Laufer et al. 1999). A significant contribution of terrestrial water by comets would still be permitted if their high D/H ratio were appropriately lowered by accretion of additional, deuterium-poor materials. Suggested possibilities for low D/H carriers include rocky planetary accretional components (Laufer et al. 1999), or a high influx during the heavy bombardment epoch of interplanetary dust particles heavily loaded with implanted solar-wind hydrogen (Pavlov et al. 1999).

Origins of volatile species on the terrestrial planets were modeled by Owen, Bar-Nun and co-workers as having resulted from accretion, in variable planet-specific proportions, of rocky materials as well as three types of comets. These formed at different heliocentric distances and thus at different nebular temperatures, leading to distinctive elemental fractionation patterns in volatiles trapped in their ices from ambient nebular gases (e.g., Owen et al. 1991, 1992; Owen and Bar-Nun 1995a,b). Present planetary inventories in such models are generated by simple mixing, in the sense that volatile abundances delivered by early cometary and rocky planetesimal bombardment are not subsequently altered by losses to space—except on Mars, where non-fractionating impact erosion has depleted volatile abundances. Suitable mixing of rocky-component volatiles with those contributed by comets formed at specific temperatures (~30 K for Venus, as noted above) can arguably reproduce relative elemental abundances of the noble gases (e.g., Fig. 3 in Owen and Bar-Nun 1995b) as well as C and N on the terrestrial planets (Owen and Bar-Nun 1995a).

The principal difficulty encountered by these mixing models in their present form is their inability to account for differences in nonradiogenic noble gas isotopic distributions between Earth and Mars, and between both of these and solar compositions (Swindle 2002; Wieler 2002), which imply processing of primordial atmospheres by isotopically fractionating mechanisms. As noted above, solar isotope ratios would be expected in the ambient nebular gases surrounding accreting cometary matter. Recent experiments

specifically designed to investigate isotopic fractionation in the gas trapping process showed maximum heavy isotope enrichments which are too small to explain planetary isotopic offsets from solar-like ratios (Notesco et al. 1999)—in particular, those displayed by $^{36}\text{Ar}/^{38}\text{Ar}$ on Mars and by Xe on both planets. Also, models that rely on supply of noble gases from material trapped in the outer parts of the solar system cannot explain the abundances of mantle noble gases, since these materials are expected to be provided as a ‘late veneer’ when accreting bodies are supplied from a wider swathe of the nebula, and are more likely to devolatilize upon impact due to the size of the proto-Earth (see “Losses during accretion” section).

Xe fractionation in porous pre-planetary planetesimals. Nonradiogenic xenon isotope ratios on Earth and Mars are grossly mass-fractionated relative to the solar Xe composition. There are two current models for the origin of planetary Xe from solar Xe. The first involves driving initially solar-like Xe compositions to their present isotopically heavy states by fractionating losses to space by hydrodynamic escape from the planets themselves. This occurs after the acquisition of noble gas inventories by unrelated process, and is discussed below. The other possibility, originally suggested by Ozima and Nakazawa (1980) (see also Ozima and Igarashi 1989) and redeveloped and extended by Zahnle et al. (1990b), is fractionation of nebular Xe into the terrestrial composition by gravitational isotopic separation in large (~Ceres-size) porous planetesimals which have now vanished from the solar system. Nebular gases are gravitationally segregated within interconnected pore spaces due to the dependence of scale height on species mass. The process terminates when growth inhibits further diffusive equilibration and loss to space. Later accretion of these bodies supplies Earth-like Xe to all three terrestrial planets. The conceptual impetus for attributing planetary Xe to a common pre-planetary source lies in the view that fractionating processes operating on individual bodies as dissimilar as Earth and Mars, and perhaps driven by power sources as different as short-term decay of energy deposited in a giant impact on Earth and long-term exposure to EUV radiation on Mars, would be unlikely to result in the qualitatively similar nonradiogenic Xe compositions in their current atmospheres (e.g., Zahnle et al. 1990b)—a similarity that, in hydrodynamic escape modeling, must be regarded as coincidental.

Isotopic fractionation of nebular Xe to obtain the terrestrial atmospheric composition can be achieved in this model, although generation of the atmospheric Xe abundance requires retention of Xe within the planetesimal by adsorption as well (Zahnle et al. 1990b). Fractionations of Kr and Ar isotopes in this process are given by Ozima and Zahnle (1993) as functions of planetesimal radius. However, while these are in the right directions, it is not clear that terrestrial isotopic compositions of all three noble gases can be generated from solar compositions, for any distribution of planetesimal masses accreted by the Earth. The highly fractionated Kr and lighter noble gases must be mixed at some point with other, unfractionated components—and, in the case of Ne, further processed by fractionating escape to space (Ozima and Zahnle 1993)—to generate the isotopic distributions displayed by these species in the present-day terrestrial atmosphere. In this respect, post-accretional atmospheric evolution on Earth is modeled in much the same way as in the hydrodynamic escape model described below, with the early, isotopically fractionated noble gas inventory deposited by accretion of porous planetesimals rather than being generated on the planet itself by hydrodynamic escape of a primary atmosphere. A consequence of this mechanism is that the atmospheric noble gas characteristics are established in accreting materials, so that noble gases presently within the deep Earth are predicted to have the same characteristics. Since this is the only model to predict isotopic ratios for primordial (i.e., not recycled) noble gases still trapped within the Earth that are fractionated relative to solar, further constraints on mantle noble gases may speak to its applicability.

This kind of model has not been applied in any detail to Mars. A problem that confronts it on that planet is the observation that Xe on Mars and Earth, while displaying comparable light-isotope ratios, is compositionally different at the heaviest isotopes in ways that cannot be explained by variable additions of ^{244}Pu or ^{238}U fission Xe to either or both atmospheres. As discussed below, it appears that Xe compositions on the two planets reflect mass fractionation of two isotopically distinct primordial starting compositions, in conflict with the hypothesis of a common planetesimal source. Venus is the key. Even a moderately accurate isotopic analysis of Venusian Xe, where no data presently exist and where the nonradiogenic Xe compositions predicted by the two models—Earth-like if supplied by porous planetesimals, and solar-like if unfractionated by hydrodynamic escape—are very different, should rule definitively between them—or create problems for both.

LOSSES AND MODIFICATIONS OF PLANETARY NOBLE GASES

As discussed above, primary volatile sources in current models for the history of terrestrial planet atmospheres may include the solar nebula, solar wind, comets, one or more known meteorite classes, or other bodies carrying different volatile distributions — with the assumption that these represent materials that either are no longer extant in the solar system or exist but are unsampled. Some of these appear likely to preserve their compositional signatures during final addition to the planets. Such presumably nonfractionating processes of incorporation into the Earth and addition to the atmosphere include impact-degassing of meteorites or cometary matter accreted by planets, direct gravitational capture of ambient nebular gases, planetary outgassing, and ejection of gases by impact of accreting bodies into preexisting atmospheres. Other mechanisms fractionate either elements alone, or both elements and isotopes. Examples are implantation and diffusion of solar wind gases in dust grains prior to accretion, adsorption of gravitationally condensed nebular gases on protoplanetary or planetary surface materials, solution of ambient volatiles into the melted surfaces of planets during accretion, partitioning in planetary interiors, and loss of atmospheric constituents from planetesimals or planetary bodies by thermal evaporation (Jeans escape) or hydrodynamic escape or by nonthermal processes such as sputtering (see below).

None of the acquisition models described above can explain all of the presently observed noble gas characteristics in the terrestrial planets, indicating that subsequent loss processes have caused further modifications.

Losses during accretion

As growth of a protoplanet proceeds with increasing accretional energy, shock-induced devolatilization of the accreting materials occurs and volatile species are transferred into the growing atmosphere. Data summarized by Ahrens et al. (1989) indicate that efficient loss of CO_2 and H_2O from accreting solids on impact occurs when its mass approaches that of Mars. Above this size (on Earth and Venus) degassing would also be driven by extensive melting due to deposition of accretional energy (Safronov 1978), and further promoted by a radiative blanketing effect if a water-rich atmosphere is accumulated (see Abe and Matsui 1986). The overall extent of this degassing depends upon the depth and duration of melting, the rate of convection, and the efficiency of degassing of material at the protoplanetary surface. While this process will facilitate transfer of noble gases to the atmosphere, it will limit how much can be buried in the growing planet.

Loss of atmospheric gases to space can occur by impact erosion, when a sufficient transfer of energy from accreting bodies occurs so that a substantial portion of the protoplanetary atmosphere reaches escape velocity (see Cameron 1983; Ahrens 1993).

For smaller accreting bodies, the maximum fraction of the atmosphere that can be expelled is $\sim 6 \times 10^{-4}$ (Vickery and Melosh 1990), equivalent to the total above the plane tangent to the planetary surface at the impact location. However, atmospheric loss may be much greater for very large impacts by bodies exceeding lunar size (Chen and Ahrens 1997). It should be emphasized that these impact-driven losses are not expected to generate elemental or isotopic fractionations in the noble gases, and contribute only to the overall depletion of these species.

A Moon-forming collision of an approximately Mars-sized body with Earth (e.g., Hartmann and Davis 1975; Cameron and Ward 1976) would clearly result in catastrophic loss of volatiles from the pre-existing atmosphere and may have caused substantial loss of deep-Earth noble gases as well. Detailed studies of atmospheric structure and dynamics during and following such an impact have not been carried out, and clearly would be a challenging task. A central issue is whether any remnant of the original atmosphere could have survived the event. Ahrens (1990, 1993), for example, argues that virtually complete expulsion might have occurred by direct ejection from the impacted hemisphere and by shock-induced outward ramming of the antipodal planetary surface. However a plausible alternative is that mechanical losses were incomplete, and may have been followed by additional losses driven by thermal processes. If so it may prove difficult to blow off the entire atmosphere, in particular its heavier constituents. Retention of a fraction of the primary pre-impact atmosphere is an important requirement in the model of terrestrial volatile evolution discussed below, where further hydrodynamic loss and fractionation of a post-impact atmospheric residue is responsible for setting the present abundance and isotopic composition of Xe.

Sputtering

Probable operation, on Mars, of an atmospheric loss mechanism that results in fractionation of elements and isotopes in the residual atmosphere was demonstrated by Luhmann et al. (1992) and Zhang et al. (1993). Oxygen atoms in the Martian exosphere, ionized by solar EUV radiation and accelerated in the motional $\mathbf{v} \times \mathbf{B}$ electric field of the solar wind, can impact species near the top of the atmosphere (the “exobase”) with enough energy transfer to eject them from the planet’s gravitational field. The exobase is defined as that atmospheric altitude where, in this case, an arriving oxygen ion would traverse one mean free path in overlying exospheric material before encountering it (Chamberlain and Hunten 1987). Loss rates of the dominant atmospheric constituent at the exobase (CO_2 on Mars) in this sputtering process depend on the magnitudes of the EUV flux and the solar wind velocity, and so estimates of how both electromagnetic and corpuscular radiation have evolved over solar history are needed in order to calculate sputtering losses in past epochs (Zhang et al. 1993)—note that this same requirement for knowledge of flux history applies to EUV-driven hydrodynamic escape as well (see next section). Escape fluxes of sputtered trace constituents in the atmosphere—e.g., noble gases and nitrogen—are proportional to their exobase mixing ratios with CO_2 (Jakosky et al. 1994).

Sputtering losses are greatly attenuated by the presence of a planetary magnetic field, most importantly because it deflects the solar wind around the planet and shields atoms photoionized in the outer atmosphere from the solar wind electric field that would otherwise accelerate some of them downward toward the exobase (Hutchins et al. 1997). For this reason the process would not have been important on Earth for as long as the core dynamo has existed, and it seems unlikely that the bulk composition of the massive Venusian atmosphere could have been substantially affected by sputtering loss with or without the protection of a paleofield. Escape of sputtered species is also impeded by the higher gravity of these two planets. In contrast, a thin, magnetically unshielded, and more

weakly bound Martian atmosphere is particularly vulnerable to sputtering erosion. Efficient operation of this fractionating loss mechanism over time on Mars is therefore centrally linked both to atmospheric pressure history and to the timing of the disappearance of the Martian paleomagnetic field (Hutchins et al. 1997; Connerney et al. 1999).

Fractionation from the sputtering process is governed primarily by the barometric law. An atmosphere is compositionally well-mixed up to an altitude called the homopause, on present-day Mars at ~ 120 km; above that point, it gravitationally separates according to $N(\Delta z) = N_H \exp[-mg\Delta z/kT]$ where N_H is the abundance of a particular species of mass m at the homopause, g is the gravitational acceleration, k is Boltzmann's constant, and Δz and T are the atmospheric altitude and temperature above the homopause. It follows directly that the abundance ratio of two species of masses m_1 and m_2 at Δz , relative to their ratio at the homopause, is $R = \exp[-\Delta m g \Delta z / kT]$, where $\Delta m = m_1 - m_2$ (Jakosky et al. 1994). If m_1 is less than m_2 , R is greater than 1; sputtering loss from the exobase therefore preferentially removes lighter species, leaving the residual atmosphere enriched in heavier constituents. These atmospheric sputtering fractionations are thus seen to be generated by loss from a fractionated "target" (the exobase). Depletions of lighter species are further augmented in the escape process itself since ejection efficiency from the exobase (atoms ejected per incident ion) increases with decreasing atomic mass (Jakosky et al. 1994).

The exponential barometric decline of abundances with increasing mass generates an enormous range of elemental fractionations at the exobase; using Jakosky et al.'s (1994) estimate of ~ 0.4 km/K for Martian $\Delta z/T$, $N(\Delta z)/N_H$ is approximately 3×10^{-2} for ^{20}Ne and 2×10^{-3} for ^{36}Ar , but 3×10^{-7} and 10^{-10} for ^{84}Kr and ^{130}Xe respectively. Sputtering loss of the two heaviest noble gases is consequently extremely small, and isotopic fractionation in the process has negligible influence on the composition of their total atmospheric inventories.

Hydrodynamic escape

Much of the evolutionary modeling over the past 15 years or so has focused on fractionation from primordial source compositions during thermally driven atmospheric escape. In the first of these, Donahue (1986) considered fractionation effects resulting from classical Jeans escape of pure, solar-composition noble gas atmospheres from large planetesimals. Their atmospheres were assumed to derive from outgassing of nebular gases previously adsorbed on the surfaces of preplanetesimal dust grains, and were subsequently fractionated to different degrees by losses that depend on the rates of planetesimal growth. These bodies later accumulated in various proportions to form the terrestrial planets and their atmospheres, and in this respect the approach is similar to that taken in the porous planetesimal model discussed above although fractionation is attributed to entirely different mechanisms in the two cases. Donahue's model can account reasonably well for relative Ne:Ar:Kr elemental abundances and for Ne isotopic compositions in the atmospheres of Venus, Earth and Mars. Predicted $^{36}\text{Ar}/^{38}\text{Ar}$ ratios, however, are much lower than observed, and variations in Kr and Xe elemental and isotopic compositions in different planetary reservoirs cannot be explained since Jeans escape of such heavy species from the parent planetesimals would have been essentially nil.

These problems are proving to be more tractable in the context of a related thermal loss mechanism, hydrodynamic escape (Zahnle and Kasting 1986; Hunten et al. 1987, 1988, 1989); Sasaki and Nakazawa 1988, 1990; Zahnle et al. 1990a; Pepin 1991, 1994, 1997, 2000). Here atmospheric loss is assumed to occur from much larger bodies, partially or fully accreted planets. Their hydrogen-rich primordial atmospheres are heated

at high altitudes, after the nebula has dissipated, by intense far-ultraviolet radiation from the young sun or alternatively, in the case of the Earth, by energy deposited in a large Moon-forming impact event. Under these conditions hydrogen escape fluxes can be large enough to exert upward drag forces on heavier atmospheric constituents sufficient to lift them out of the atmosphere. Lighter species are entrained and lost with the outflowing hydrogen more readily than heavier ones, leading to mass fractionation of the residual atmosphere. Hydrogen escape fluxes high enough to sweep out and fractionate atmospheric species as massive as Xe require energy inputs roughly two to three orders of magnitude greater than presently supplied to planetary exospheres by solar extreme ultraviolet (EUV) radiation—implying large but not prohibitive enhancements of surface activity on the early Sun. Hydrodynamic escape is particularly attractive for its ability to generate, in an astrophysically plausible environment, large isotopic fractionations with respect to solar Xe of the type displayed both by terrestrial xenon—first observed and attributed to an (unknown) fractionation process 40 years ago (Krummenacher et al. 1962)—and by Xe in the atmosphere of Mars (Swindle et al. 1986; Swindle 2002, this volume).

The potential power of the hydrodynamic loss mechanism, given adequate supplies of hydrogen and energy, to replicate observed isotopic distributions was well illustrated by Hunten et al.'s (1987) applications of the process to several specific cases, including the derivation of terrestrial Xe from solar Xe; by Sasaki and Nakazawa's (1988, 1990) independent treatment of the terrestrial Xe problem; and by Zahnle et al.'s (1990a) consideration of Ne and Ar compositions on Earth and Mars. Pepin (1991, 1994, 1997) assessed its more general viability as an actual instrument of volatile evolution by examining the consequences of hydrodynamic escape for the full range of elemental and isotopic mass distributions found in contemporary planetary atmospheres, and exploring the astrophysical and planetary conditions under which the process could account for this data base.

Historians of the field will recognize that it has come full circle with the recent emphasis on fractionation of atmospheric noble gases by escape from gravitational potential wells. This was just the approach taken by Brown (1949) and Suess (1949) in their pioneering attempts to account for the differences between the elemental abundance patterns of solar and terrestrial noble gases. A quote from a review of this early work by Signer and Suess (1963) makes the point: "All but a fraction of about 10^{-7} of the noble 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 noble gases is selective loss from a gravitational field during a limited period of time (Suess 1949)." At that time the theoretical framework of the hydrodynamic escape mechanism had not been developed, and the appeal was to classical Jeans escape, which required the fractionating loss to take place from small preplanetary planetesimals. Nevertheless this perception of evolutionary processing has a distinctly modern ring.

Theory. Theories of mass fractionation in hydrodynamic escape of gases from planetary atmospheres have been constructed by Zahnle and Kasting (1986) and by Hunten et al. (1987). Hunten et al.'s (1987) relatively simple analytic approach assumes the presence of an isothermal atmosphere consisting of an abundant light gaseous species and minor amounts of heavier components. Energy input at high altitudes drives thermal loss of the light constituent with escape flux F_1 particles $\text{cm}^{-2} \text{sec}^{-1}$. The escaping gas exerts upward drag forces on heavier species. For a given F_1 the drag is sufficient to lift all constituents with masses m_2 less than a critical mass m_c out of the atmosphere. Analytic expression of the theory (Hunten et al. 1987; Pepin 1991, 1997), for an

atmosphere containing inventory N_1 of the abundant light species with mass m_1 (constituent 1) and inventories N_2 of trace species with masses $m_2 > m_1$ (constituents 2), leads to escape fluxes F_2 of the minor, heavier constituents given by

$$F_2 = F_1 \frac{N_2}{N_1} \left[\frac{m_c - m_2}{m_c - m_1} \right] \quad (2)$$

for $m_c \geq m_2$. The critical or “crossover mass” m_c in Equation (2), representing the smallest mass for which the escape flux F_2 of a particular mass m_2 in constituent 2 is zero, is defined (Hunten et al. 1987) as

$$m_c = m_1 + \frac{kTF_1}{bgX_1} \quad (3)$$

where k = Boltzmann’s constant, T = atmospheric temperature, g = gravitational acceleration, X_1 is the mole fraction of the abundant constituent 1 (assumed to remain near unity throughout the escape episode), and b is the diffusion parameter (the product of diffusion coefficient and total number density) of mass m_2 in the constituent 1 gas. Note from Equation (3) that a large F_1 yields a large crossover mass m_c ; for F_1 high enough that $m_c \gg m_2 > m_1$, losses described by Equation (2) are maximum (atmospheric “blowoff”) and species in constituent 2 escape close to the ratios N_2/N_1 of their atmospheric inventories—i.e., without fractionation. Maximum fractionation occurs when F_1 drops to the level where m_c approaches m_2 .

Constituent 1 is usually assumed to be molecular hydrogen. Constituent 2 is taken to be a multicomponent noble gas mixture—excluding He, which is only weakly bound in terrestrial planet atmospheres and escapes readily by other processes. The diffusion parameter b in Equation (3), and thus the crossover mass m_c , differs for different elements S in constituent 2. If $m_c(S)$ is known (or assumed) for one element, say Xe, then Equation (3) for both Xe and S yields

$$m_c(S) = m_1 + [m_c(\text{Xe}) - m_1] \left[\frac{b(\text{Xe})}{b(S)} \right] \quad (4)$$

for the S crossover mass, where S represents Kr, Ar or Ne. Values of $b(S)$ for noble gas diffusion in H_2 at various temperatures are known (Mason and Marrero 1970; Zahnle and Kasting 1986). They increase from Xe to Ne by a factor of approximately 2 that varies only slightly with temperature, and are identical or nearly so for isotopes of a given element.

The energy required for escape of a particle with mass m_1 from its local gravitational field, at radial distance $r \geq r_s$ from a body of mass M and radius r_s , is Gm_1M/r ergs per particle. If the global mean solar EUV input at heliocentric distance R and time t is $\phi(R,t)$ ergs $\text{cm}^{-2} \text{sec}^{-1}$, the energy-limited escape flux is

$$F_1(R,t) = \frac{\phi(R,t)\epsilon}{Gm_1M/r} = \frac{r\phi(R,t)\epsilon}{Gm_1M} \quad \text{particles cm}^{-2}\text{sec}^{-1} \quad (5)$$

where ϵ is the fraction of incident EUV energy flux converted to thermal escape energy of m_1 . Energy input ϕ may be expressed in terms of the current mean EUV flux at Earth $\phi_{\oplus}(t_p)$, heliocentric distance R , and the ratio Φ_{EUV} of the flux at past time t to that at present time t_p . Defining $\phi(R,t_p) = (R_{\oplus}/R)^2 \phi_{\oplus}(t_p)$ and $\Phi_{\text{EUV}}(t) = \phi(R,t)/\phi(R,t_p)$ yields $\phi(R,t) = (R_{\oplus}/R)^2 \phi_{\oplus}(t_p) \Phi_{\text{EUV}}(t)$. Substituting this into Equation (5) and combining Equations (5) and (3), with $g = GM/r^2$ and M expressed in terms of r_s and planetary density ρ , yields

$$m_c(S) = m_1 + \left(\frac{3}{4\pi G \rho}\right)^2 \left(\frac{1}{r_s}\right)^3 \left(\frac{R_\oplus}{R}\right)^2 \left(\frac{kT}{X_1}\right) \left(\frac{\phi_\oplus(t_p)\mathcal{E}}{b(S)m_1}\right) \left(\frac{r}{r_s}\right)^3 \Phi_{\text{EUV}}(t) \quad (6)$$

relating crossover masses of minor species S to the EUV flux irradiating a planetary atmosphere at heliocentric distance R. It can be seen here that once the history of the driving energy source for loss, i.e., the EUV flux, is known, and assumptions are made about the initial inventory and ongoing supply of the major volatile species, H₂, the losses of each species can be calculated.

Information on what $\Phi_{\text{EUV}}(t)$ might have been in the early solar system comes from astronomical observations of radiation from young solar-type stars at various stages of pre- and early-main-sequence evolution. Since early solar EUV radiation could not have penetrated a full gaseous nebula to planetary distances, the applicable time dependence of stellar activity in the present model is that following dissipation of the dense accretion disks surrounding the classical T-Tauri stars at stellar ages of up to ~10 Ma (Walter et al. 1988; Strom et al. 1988; Walter and Barry 1991; Podosek and Cassen 1994). Among present observational data, soft (~3 to 60 Å) X-ray fluxes are most likely to be representative of at least the short-wavelength coronal component ($\lambda < 700$ Å) of the EUV spectrum. Figure 10 shows X-ray luminosities L_X , relative to that of the present sun, from observations of T-Tauri stars without disks (the “Weak T-Tauri Stars”: Walter et al. 1988) and older solar-type main-sequence field stars (Simon et al. 1985), plotted against estimates of stellar ages (Walter and Barry 1991). Although considerable scatter from a single functional dependence of Φ_X on age is evident, most of the data for t between ~50 and 200 Ma do indicate a decline by factors of ~5-10 from levels at ~20 Ma.

In current escape models (Pepin 1991, 1994, 1997), Φ_{EUV} is assumed to fall off exponentially, with a mean decay time τ of 90 Ma, along the dashed curve in Figure 10; the solid portion of the curve identifies the period of interest for EUV-driven loss of planetary atmospheres. An alternative, power law function for $\Phi_X(t)$ of the type suggested by Feigelson and Kriss (1989) is also plotted. Models of hydrodynamic escape analogous to those for exponential flux decay have been constructed for this kind of power law dependence (Pepin 1989). Results are similar enough to indicate that the particular mathematical form of the decay in stellar flux through the period of atmospheric evolution is not centrally important. Decline of the EUV flux over the first few hundred Ma of solar history, by roughly the factor suggested by present astronomical data, is a crucial requirement of the modeling because, from Equation (6), it results in declining crossover masses to the level where fractionations described by Equation (2) and calculated below are large enough to match Xe isotopic distributions in current atmospheres.

In the case where energy deposited in an atmosphere by EUV radiation or from some other source declines exponentially with time, the flux F_1 of constituent 1 is given by

$$F_1 = F_1^0 \exp\left[\frac{-(t-t_0)}{\tau}\right] \quad (7)$$

where F_1^0 is the initial escape flux at t_0 and τ is the mean decay time of the energy source. Equation (3) then requires the crossover mass $m_c(S)$ to decrease as well, from its initial value $m_c^0(S)$ at time t_0 and flux F_1^0 to its final value $m_c^f(S)$ at time t_f when escape either terminates due to hydrogen depletion or undergoes a transition to diffusion-limited hydrogen escape through a atmosphere of increasing molecular weight; in this latter case only Ne and perhaps Ar will continue to be lost (see Zahnle et al. 1990a). If $m_c(S)$ declines through the mass m_2 of a trace species S, loss of m_2 ends when $m_c(S) = m_2$ but escape of lighter isotopes or elements continues for as long as the $m_c(S)$ for each specific constituent is greater than its particular mass.

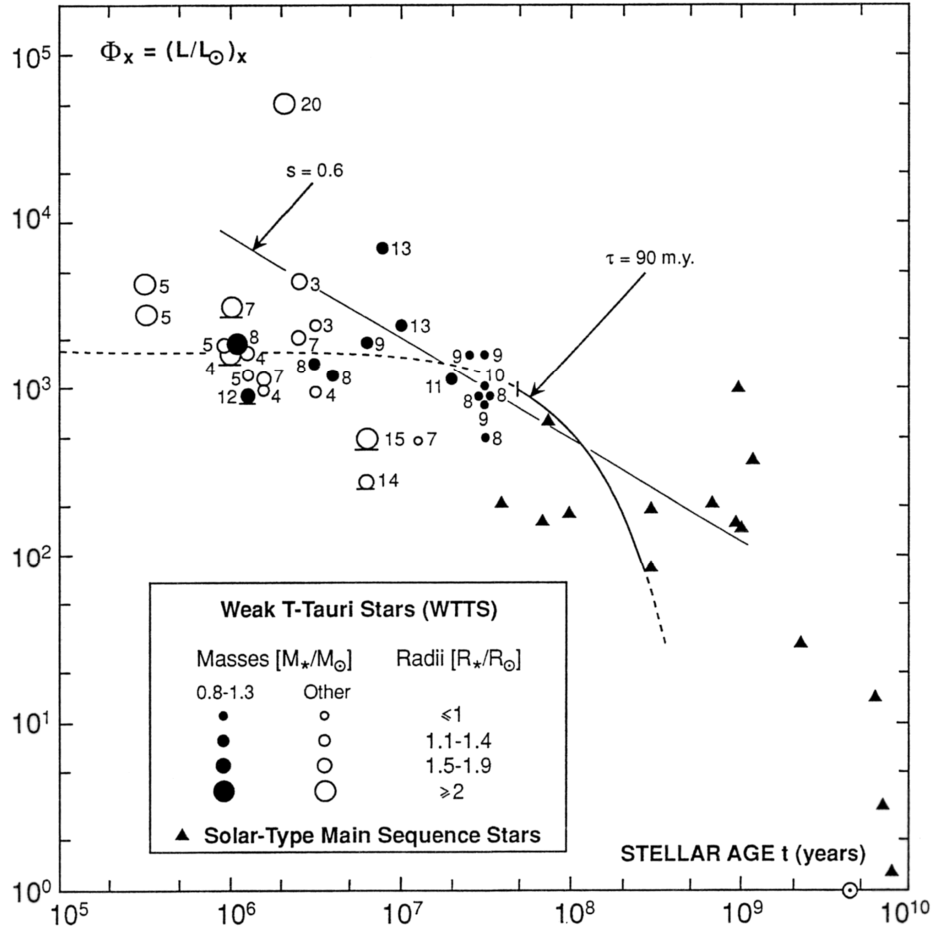


Figure 10. Observed X-ray luminosities L_X relative to the present sun vs. stellar ages for "weak-lined" T-Tauri stars (WTTS) and solar-type main sequence stars (MSS) (Pepin 1991). All WTTS data are from Walter et al. (1988), MSS data from Simon et al. (1985) and Walter and Barry (1990). Numbers adjacent to the plotted WTTS points are stellar mass estimates in tenths of a solar mass. Underlined symbols identify measurements that yielded only lower limits on luminosity. In the models explored in the text, both soft X-ray (Φ_X) and EUV (Φ_{EUV}) luminosity enhancements are taken to decline exponentially with a mean decay time $\tau = 90$ Ma over the period of interest for planetary atmospheric evolution (indicated by the solid portion of the plotted curve). A $\Phi_X \propto (1/t)^s$ power law decay with $s = 0.6$ (Feigelson and Kriss 1989) is shown for comparison.

Fractionating effects of the escape process can now be calculated analytically if specific assumptions are made about the time dependence of the major (constituent 1) inventory N_1 —that it is either replenished as fast as it escapes (constant inventory model), or is lost without replenishment along with the minor atmospheric species (Rayleigh fractionation model). In both cases the inventories N_2 of minor species, here the noble gases, are assumed to be in the atmosphere at t_0 and are lost without replenishment during the escape episode. For Rayleigh fractionation, adopted for this discussion, Equations (2), (3), and (7) and the definitions $F_1 = -dN_1/dt$ and $F_2 = -dN_2/dt$ may be combined and integrated, in the limit of $X_1 \cong 1$, $m_c^0 > m_2 > m_1$, and $m_c^f \geq m_2$, to yield

$$\ln \frac{N_2^f}{N_2^o} = \ln \frac{N_1^f}{N_1^o} + \frac{\alpha_o}{1 - \alpha_o} \left[\frac{m_2 - m_1}{m_c^o - m_1} \right] \ln \left[\frac{N_1^f}{N_1^o} \frac{m_c^o - m_1}{m_2 - m_1} \right] \quad (8)$$

for the fractional depletion of a particular minor species of mass m_2 (Hunten et al. 1987;

Pepin 1991). N_1^0, N_1^f and N_2^0, N_2^f are the initial and final inventories of the major and minor constituents. The dimensionless parameter α_0 is defined as $\alpha_0 = F_1^0 \tau / N_1^0$. The fractional retention of constituent 1 at t_f is given by

$$\frac{N_1^f}{N_1^0} = 1 - \alpha_0 \left[\frac{m_c^0 - m_c^f}{m_c^0 - m_1} \right] \quad (9)$$

(Pepin 1991). From the definitions of m_c (Eqn. 3) and α_0 , the initial inventory of constituent 1 is

$$N_1^0 = \frac{bgX_1(m_c^0 - m_1)\tau}{kT\alpha_0} \text{ particles cm}^{-2}. \quad (10)$$

The total duration $t_f - t_0$ of the escape episode is related to mean energy decay time and the initial and final crossover masses by

$$t_f - t_0 = -\tau \ln \left[\frac{m_c^f - m_1}{m_c^0 - m_1} \right]. \quad (11)$$

Note that equations containing t involve only time differences, not their absolute values (e.g., Eqns. 7 and 11). Consequently the fractionations of initial isotopic and elemental ratios generated by hydrodynamic escape do not depend on any specific choice for t_0 , the time in solar evolutionary history when atmospheric escape begins. Permitted values of t_0 are constrained, however, by the solar EUV flux needed to drive an escape episode. For example, as noted in the following section, EUV-driven Xe loss from Earth requires a flux that exceeds the present solar level by a factor of ~ 450 , and thus a t_0 no later than ~ 100 Ma if the flux history follows the $\tau = 90$ Ma exponential in Figure 10. It is assumed that t_0 , whatever its value, marks the time at which dust and gas in the nebular midplane had cleared to the extent that solar EUV radiation could penetrate to planetary distances, so that EUV-driven atmospheric loss would not have occurred prior to t_0 (Prinn and Fegley 1989).

Isotopic and elemental fractionations generated in constituent 2 residues are calculated from separate solutions of Equation (8) for particular choices of mass m_2 and a reference mass $[m_2]_{\text{ref}}$. Then $(N_2/N_2^0)/([N_2/N_2^0]_{\text{ref}}) = \{N_2/[N_2]_{\text{ref}}\}/\{N_2^0/[N_2^0]_{\text{ref}}\}$ is the corresponding fractionation factor. For example, if S is xenon and the inventories $N_2(S)$ and $[N_2(S)]_{\text{ref}}$ are respectively taken to represent ^{124}Xe and ^{130}Xe , the isotopic fractionation is $(^{124}\text{Xe}/^{124}\text{Xe}^0)/(^{130}\text{Xe}/^{130}\text{Xe}^0) = (^{124}\text{Xe}/^{130}\text{Xe})/(^{124}\text{Xe}/^{130}\text{Xe})^0$ where $(^{124}\text{Xe}/^{130}\text{Xe})^0$ is the original (unfractionated) ratio.

Adjustable modeling parameters include the mass m_1 of the abundant light constituent (taken to be H_2 in most models); atmospheric temperature T ; initial crossover mass m_c^0 for one noble gas—for example, for m_c^0 (Xe) as in Equation (4)—and its lower value m_c^f for the same species when the loss episode terminates (crossover masses for the remaining trace gases are fixed by Eqn. 4), which with m_1 , T , and $b(S)$ sets the initial value of F_1 via Equation (3); the decay constant τ for the thermal energy supply; the parameter $\alpha_0 = F_1^0 \tau / N_1^0$ which for a given τ sets the initial ratio of escape flux to inventory for H_2 ; and the isotopic and elemental ratios of noble gases in the initial primordial atmosphere. It's important to note that allowed parameter space is not unconstrained. In Equation (9), for example, the light constituent abundance N_1 cannot be negative; N_1^f/N_1^0 must therefore be ≥ 0 , which limits the permitted combinations of α_0 and m_c^f values for a particular choice of m_c^0 .

With suitable choices of parameter values, hydrodynamic escape of hydrogen-rich primary atmospheres and outgassed volatiles from the terrestrial planets (plus sputtering

losses on Mars), operating in an astrophysical environment for the early solar system inferred from observation of young star-forming regions in the galaxy and from models of planetary accretion, can account for most of the known details of noble gas distributions in their present-day atmospheres. The question, of course, is whether the required values or ranges of values required for the free modeling parameters reflect realistic astrophysical and planetary conditions in the early history of the solar system. The conditions required on each planet for obtaining the observed noble gas characteristics are described in the following sections.

Application to Earth. Current modeling requires the Earth to have acquired two isotopically primordial volatile reservoirs during accretion, one in the planet's interior, perhaps populated by a combination of nebular gases occluded in planetary embryo materials and dissolved in molten surface materials, and the other coaccreted as a primary atmosphere degassed from impacting planetesimals or gravitationally captured from ambient nebular gases during later planetary growth. These "isotopically primordial" reservoirs are characterized by isotope ratios measured in the solar wind, with the important exception of Xe; here the U-Xe composition, which differs substantially from solar wind Xe at the two heaviest isotopes, is required (see Fig. 7 and discussion in the "Terrestrial noble gases" section). Evolutionary processing proceeds in two stages. In the first stage, substantial depletion of Xe from the primary atmosphere occurs, driven by deposition of atmospheric energy. This sets the Xe inventory and generates the extensive Xe isotopic fractionation that is presently observed in the terrestrial atmosphere. However, the other, lighter noble gases are greatly overdepleted at the end of the first stage. Subsequently, mixing of the fractionated atmospheric residue with species degassed from the second, interior reservoir compensates for the overfractionation of Kr, Ar, and Ne elemental and isotopic abundances in the first stage, and produces the presently observed distributions of these gases. Modeling must therefore aim to define not only the hydrodynamic escape parameters that generate terrestrial Xe, but also the relative elemental abundances in both the primary atmospheric and interior reservoirs required to produce the final composition of the other noble gases.

In the original formulation of the model (Hunten et al. 1987; Pepin 1991), hydrodynamic losses of primary atmospheric volatiles are driven by intense EUV radiation from the young evolving Sun. Hydrogen outflow fluxes strong enough to enable Xe escape from Earth, and fractionation to its present isotopic composition, required atmospheric H₂ inventories equivalent to water abundances of up to a few wt.% of the planet's mass, and early solar EUV fluxes up to ~450× present levels—large but, as seen in Figure 10, not unrealistic enhancements if nebular dust and gas had dissipated to levels low enough for solar EUV radiation to penetrate the midplane to planetary distances within 100 Ma or so.

Energy sources other than solar EUV absorption may have powered atmospheric escape. Benz and Cameron (1990) suggested that hydrodynamic loss driven by thermal energy deposited in a giant Moon-forming impact could have generated the well-known fractionation signature in terrestrial Xe. Their model of the event calls for rapid invasion of the pre-existing primary atmosphere by extremely hot (~16,000 K) dissociated rock and iron vapor, emplacement of an orbiting rock-vapor disk with an inner edge at an altitude comparable to the atmospheric scale height at this temperature, and longer-term heating of the top of the atmosphere by reaccretion of dissipating disk material.

As yet there are no detailed theoretical calculations supporting the proposition that the physical conditions and energy-decay timescale needed to implement hydrodynamic escape could have been met in the aftermath of a giant impact on Earth. If a short post-impact escape episode did in fact occur, resulting in Rayleigh fractionation of whatever

remnant of the primary atmosphere survived direct—and presumably non-fractionating—ejection in the impact event, required atmospheric H₂ inventories would be reduced by an order of magnitude or more compared to models in which losses are driven only by solar EUV radiation (Pepin 1997); this is in part a consequence of the scaling of N_1^0 with the energy decay constant τ in Equation (10), where, as noted below, τ for post-impact energy dissipation is assumed to be small. EUV-powered escape is still needed at some time following the impact event to account for Ne isotopic distributions (see below), but flux intensities for Ne-only loss are also about an order of magnitude lower than those required to lift heavier noble gas species out of the atmosphere. With appropriate choices for free parameters, both this and the original EUV-only model (Pepin 1991) can generate close matches to noble gas elemental and isotopic distributions in the contemporary terrestrial atmosphere.

The interplay of atmospheric escape fractionation and subsequent degassing required to achieve these matches is illustrated for the hybrid giant impact (GI)-EUV model in Figure 11. The mean decay time τ of energy deposited by the impact is presumably small, reflecting relatively rapid energy dissipation following the event: here τ is arbitrarily chosen to be 1000 years, and with this and other model parameter values, Equation (11) yields an escape episode that runs its course in a comparable time. Primordial atmospheric U-Xe is fractionated by GI-driven hydrodynamic escape to its present abundance and nonradiogenic isotope ratios. About 85% of the initial ¹³⁰Xe inventory is lost from the planet. The resulting “nonradiogenic Earth atmosphere” is used in Figure 11 as the Xe reference composition. Post-escape isotopic evolution of atmospheric Xe is largely restricted to degassing of radiogenic ¹²⁹Xe, and of ¹³¹⁻¹³⁶Xe generated primarily by spontaneous fission of ²⁴⁴Pu, from the upper mantle and crust (see Fig. 13, below). This constraint on “pollution” of the nonradiogenic Xe isotopic distribution generated by hydrodynamic escape, either by subsequent degassing of solar Xe from the interior reservoir or by substantial addition of isotopically different Xe carried in later-accreting material, is central to the modeling (see discussion below in *Outstanding Issues*).

Increasingly severe fractionations of the lighter noble gases from their primordial isotopic compositions are imposed by the parameter values for GI-driven Xe escape. Residual Kr and Ar are both isotopically heavy (Fig. 11) and strongly depleted relative to the present atmosphere; only 6% and 0.8% respectively of the initial ⁸⁴Kr and ³⁶Ar inventories (and 0.4% of the ²⁰Ne) survive the event. Subsequent mixing of these residues of the primary atmosphere with solar-composition Kr and Ar degassed from the interior reservoir raises their abundances to present-day values, and yields generally good ($\geq 1\sigma$) matches to contemporary isotopic compositions except for a $\sim 2\%$ (3σ) excess of ⁸⁶Kr.

Neon is a special case in that ²⁰Ne/²²Ne and ²¹Ne/²²Ne ratios in the fractionated residual atmosphere are substantially higher than at present, and later addition of outgassed solar Ne elevates them still more (Fig. 11). Here an episode of solar EUV energy deposition driving hydrodynamic escape of Ne at some time after GI fractionation and outgassing is needed to generate the contemporary ²⁰Ne/²²Ne ratio. But, as noted above, the EUV-driven H₂ escape flux must now be only intense enough to lift Ne, but not the heavier noble gases, out of the atmosphere. The waning solar EUV flux (Ayres 1997) may still have been sufficiently high ($\sim 60\times$ present levels) to drive Ne-only escape at solar ages up to ~ 250 Ma (Fig. 10), with the actual timing—somewhere in the interval between Ne degassing and ~ 250 Ma—determined by the timescale for sufficient reduction of EUV dust-gas opacity in the nebular midplane (Prinn and Fegley 1989). Note from Figure 11 that EUV escape fractionation yielding a match to the present ²⁰Ne/²²Ne ratio overfractionates ²¹Ne/²²Ne by a few percent, implying a ²¹Ne deficit in

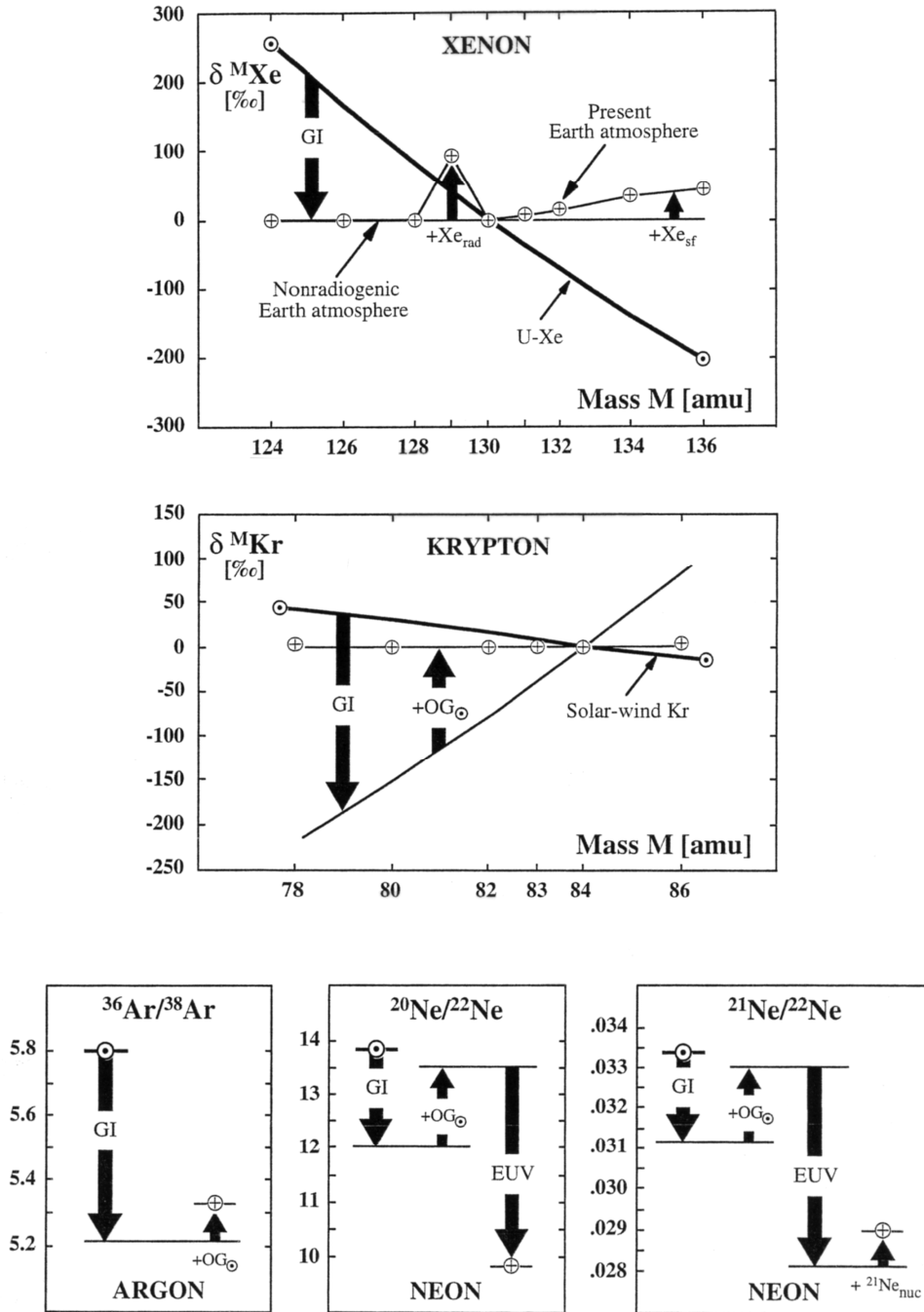


Figure 11. Evolution of terrestrial Xe, Kr, Ar and Ne from primordial atmospheric distributions to present-day compositions by Giant Impact (GI)-driven fractionation, addition of outgassed (OG) solar Kr, Ar and Ne, a later stage of solar EUV-powered Ne escape fractionation, and subsequent outgassing of radiogenic and fissionogenic Xe and nucleogenic ^{21}Ne (after Pepin 1997). The $\delta^M \text{Xe}$ and $\delta^M \text{Kr}$ representations are defined by $\delta^M = 1000 [(R/R_{\text{ref}}) - 1]$ %; here $R = {}^M \text{Xe}/^{130}\text{Xe}$ and ${}^M \text{Kr}/^{84}\text{Kr}$ respectively, and the references R_{ref} are the corresponding isotope ratios in the nonradiogenic Earth atmosphere for Xe (Pepin 1991) and the present Earth atmosphere (Basford et al. 1973) for Kr. Xe data from Table 1; solar and atmospheric Kr from Wieler (2002, Table 5, refs. 2 and 4); solar $^{36}\text{Ar}/^{38}\text{Ar} = 5.80 \pm 0.06$, $^{20}\text{Ne}/^{22}\text{Ne} = 13.84 \pm 0.04$, and $^{21}\text{Ne}/^{22}\text{Ne} = 0.0334 \pm 0.0003$ from Palma et al. (2002).

the modeling. The atmospheric abundance of ^{21}Ne , however, is subsequently augmented by outgassing over geologic time of a nucleogenic $^{21}\text{Ne}_n$ component generated primarily by $^{18}\text{O}(\alpha,n)^{21}\text{Ne}_n$ reactions in the Earth's crust and mantle (Wetherill 1954). Estimates of the fractional abundance of $^{21}\text{Ne}_n$ in the present atmosphere are consistent with the amount needed to elevate the initially lower $^{21}\text{Ne}/^{22}\text{Ne}$ ratio in Figure 11 to its present value by post-escape degassing (see Porcelli and Ballentine 2002, this volume).

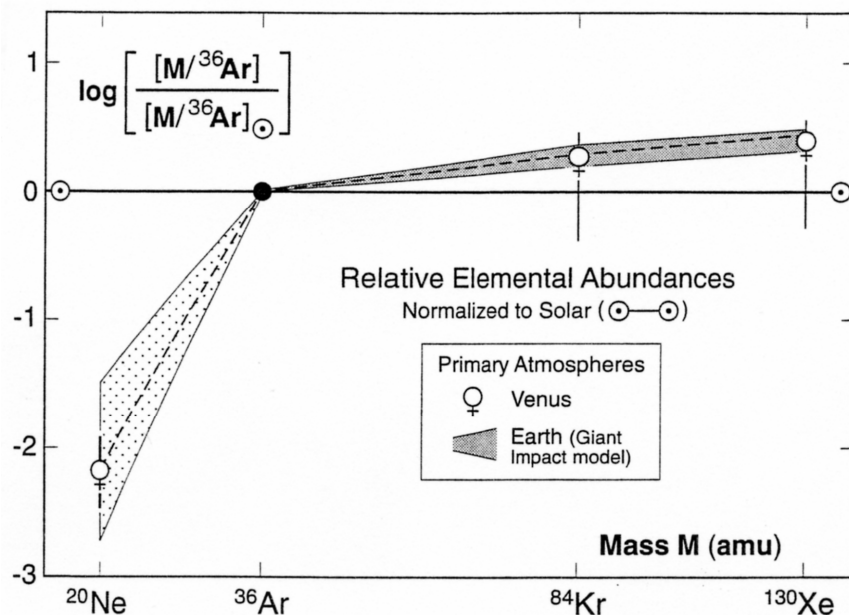


Figure 12. Modeling results for the elemental compositions of primary atmospheres on Earth and Venus, plotted relative to solar abundance ratios. The baseline model for impact-driven escape from Earth (dashed line) assumes H_2 loss from a 2000-K atmosphere. Different assumptions for atmospheric temperature and the identity of the abundant escaping constituent generate the shaded spread in Kr/Ar and Xe/Ar ratios originally present on Earth (see text). The stippled region represents the factor of ~ 5 range in initial terrestrial $^{20}\text{Ne}/^{36}\text{Ar}$, on either side of the Venus ratio, for which the Ne isotopic matches shown in Figure 1 can be generated by EUV-driven loss. All elemental data are from Pepin (1997).

Primordial heavy noble gas abundances, calculated from present inventories backward through the degassing and escape stages of evolution, yield the dashed-line relative abundance pattern shown in Figure 12 for the $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ ratios present in the pre-impact Earth atmosphere. Estimating the initial ^{20}Ne abundance on Earth is complicated by the terminal EUV-driven Ne fractionation stage. In calculating the Ne isotopic evolution shown in Figure 11 and the dashed-line elemental pattern in Figure 12, initial ^{20}Ne was assumed for illustration to be present in the same ratio relative to ^{36}Ar as in Venus' primary atmosphere (see below). Solutions yielding final Ne isotope ratios identical to those in Figure 11 exist, with differing EUV fractionation parameters and amounts of degassed $^{21}\text{Ne}_n$, for primordial atmospheric $^{20}\text{Ne}/^{36}\text{Ar}$ ranging from $\sim 1/5$ to 5 times the Venus ratio (stippled area in Fig. 12).

These modeling results assume an atmospheric temperature $T = 2000$ K and H_2 as the abundant hydrodynamically escaping species. Neither choice would be appropriate for escape from a very hot dissociated atmosphere, an environment likely to have characterized early stages of giant-impact-driven loss. However the results are not sensitive to either temperature or the exact identity of the carrier gas. The shaded area in

Figure 12 represents the relatively small spread in initial elemental composition introduced by assuming atmospheric temperatures ranging from 300 K to 10,000 K and, at temperatures ≥ 4000 K, H or O rather than H_2 as the dominant light atmospheric constituent.

Application to Venus. Data from in situ compositional measurements of the Venus atmosphere by mass spectrometers and gas chromatographs on the Pioneer Venus and Venera spacecraft are reviewed and assessed by von Zahn et al. (1983); an updated summary is set out in Table 8 of Wieler (2002). One might suspect that planets as alike as Earth and Venus in size and heliocentric distance would have acquired compositionally similar primary atmospheres from similar sources. It is not obvious, however, from comparison of volatile mass distributions on Earth and Venus, that these two atmospheres are end products of similar evolutionary processes acting on similar primordial volatile sources. Absolute abundances on Venus exceed those on Earth by a factor >70 for ^{36}Ar , but only by factors of ~ 3 -6 for Kr and Xe. Consequently, as noted above, there is a pronounced solar-like signature in relative Ar:Kr:Xe abundances. This similarity does not extend to Ne: the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio is low, close to terrestrial. Venusian $^{20}\text{Ne}/^{22}\text{Ne}$, however, is significantly higher (i.e., more solar-like) than on Earth, and the nominal value of the $^{36}\text{Ar}/^{38}\text{Ar}$ ratio is somewhat above the terrestrial value. There are no measurements of Kr and Xe isotopic compositions.

Since volatile compositions on Venus are known only approximately, if at all, isotopic constraints on modeling parameter values are much weaker than in the terrestrial case, and for the heavy noble gases are missing entirely. However the EUV flux driving Ne escape in the Earth model discussed in the preceding section must also irradiate Venus at the same time—i.e., $\Phi_{\text{EUV}}(t)$ in Equation (6) is the same for both planets—and this planetary interdependence together with the isotopic and elemental information we do have allows construction of at least a preliminary model for Venusian volatile evolution. If EUV heating efficiencies and H_2 escape altitudes are assumed to be similar, it is seen from Equation (6) that the ratio of the crossover mass $m_{\text{C}}(\text{S})$ on Venus to that on Earth for the same species is a function only of relative planetary radii, densities, heliocentric distances, and atmospheric temperatures. It turns out that the relatively weak solar EUV flux needed for Ne-only loss from Earth is still strong enough at Venus' orbital position to drive outflow of Kr and lighter gases from this smaller and less dense planet. But $m_{\text{C}}(\text{Xe})$ on Venus falls below the mass of the lightest Xe isotope, and so Venusian Xe is not lost and its nonradiogenic isotopic composition, presently unknown, is predicted to be unaltered from its primordial composition.

Results of this model of EUV-driven loss of an isotopically solar and elementally near-solar primordial atmosphere from Venus are sensitive to only one of the few remaining adjustable modeling parameters— α_0 , which fixes the initial H_2 inventory N_1^0 via Equation (10). A single value of this parameter generates matches well within their 1σ uncertainties to the very limited isotopic data we currently have for Venus' present-day noble gases ($^{20}\text{Ne}/^{22}\text{Ne}$ and $^{36}\text{Ar}/^{38}\text{Ar}$ only: see Table 8 in Wieler 2002, this volume). It is interesting that there is no discernible evidence in the data on hand that outgassing has played a significant role in establishing contemporary noble gas inventories. Fractionating loss of the primary atmosphere, governed by the parameters above, generates by itself approximate matches to observed compositions. Thus, in contrast to the case for Earth, the presence of an outgassed component on Venus is not required. This is not to say that the planet could not have degassed at some time during or after this stage of atmospheric evolution. But outgassed species would comprise only modest fractions of the large present-day Venusian atmospheric inventories even if bulk planetary concentrations were comparable to those on Earth. In fact, the atmospheric

abundance of ^{40}Ar suggests that outgassing rates on Venus have been substantially less than terrestrial rates (see “Noble gases on Venus” section).

Elemental ratios characterizing the primary (pre-loss) Venus atmosphere in this evolutionary model are plotted in Figure 12. Although these computed primordial $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ ratios inherit the large uncertainties associated with measurements of present Venusian abundances, their nominal values fall squarely within the range of estimates calculated above for Earth’s pre-impact primary atmosphere—a strong implication that noble gases on both planets could have evolved, clearly in quite different ways, from the same primordial distributions in the same types of primary planetary reservoirs. This result seems reasonably robust, provided of course that fractionating, GI-driven hydrodynamic escape actually did occur on Earth. However a central test which the Venus model must eventually confront is whether its predicted Xe and Kr isotopic compositions, respectively unfractionated and slightly fractionated with respect to primordial atmospheric compositions, are in accord with future measurements. Venus appears to represent an extreme in the range of atmospheric compositional patterns displayed by the terrestrial planets, and, as discussed below in “Outstanding Issues”, this and other central questions could be answered, or at least more quantitatively addressed, if we can eventually manage to revisit the planet for moderately accurate in situ measurements of all noble gas isotopic distributions, or, even better, return an atmospheric sample to Earth for laboratory study.

Application to Mars: losses by hydrodynamic escape and sputtering. Information about volatile abundances and compositions on and in Mars come from in situ measurements by Viking spacecraft instruments and, by a great stroke of fortune, from high-precision laboratory analyses of Martian atmospheric gases trapped in the SNC meteorites (Swindle 2002, this volume). Early modeling of the history of noble gases on Mars based on these data suggested that they could have evolved from primordial to present-day distributions through two early episodes of hydrodynamic atmospheric escape (Pepin 1991). This model, however, did not address a number of processes that now appear germane to Martian atmospheric history. One, gas loss and fractionation by sputtering, was later proposed to be the dominant mechanism governing atmospheric CO_2 evolution on Mars over the past ~3-4 Ga (Luhmann et al. 1992; Zhang et al. 1993). Another, atmospheric erosion (Melosh and Vickery 1989), appears increasingly important (Chyba 1990, 1991; Zahnle 1993). In the absence at that time of a plausible mechanism, the possibility of isotopic evolution of noble gases heavier than Ne after the termination of hydrodynamic escape was not considered by Pepin (1991), and only qualitative attention was paid to the eroding effects of impact on abundances of all atmophilic species prior to the end of heavy bombardment ~3.8 to 3.7 Ga ago.

The more recent models of Martian atmospheric evolution constructed by Jakosky et al. (1994) and Pepin (1994) incorporate the sputtering loss mechanism proposed by Luhmann et al. (1992) and Zhang et al. (1993), and explore its consequences for elemental and isotopic fractionation of the noble gas and nitrogen in the residual atmosphere. They divide Martian atmospheric history into early and late evolutionary periods, the first characterized by an initial episode of hydrodynamic escape that sets the Martian Xe inventory (discussed later in the “Primordial Xenon” section), followed by high CO_2 pressures and a possible greenhouse, and the second by either a sudden transition to a low pressure environment similar to present-day conditions on the planet—perhaps initiated by abrupt polar CO_2 condensation ~3.7 Ga ago (Gierasch and Toon 1973; Haberle et al. 1992, 1994)—or by a more uniform decline to present pressure. Jakosky et al. (1994) focused on the late evolutionary epoch, and showed that contemporary Ne, Ar and N_2 abundances and isotope ratios—including the uniquely low

Martian $^{36}\text{Ar}/^{38}\text{Ar}$ ratio (Swindle 2002, this volume)—could have been generated by sputtering losses from an atmosphere that was continuously replenished by degassing of meteoritic (CI) N_2 and isotopically solar Ne and Ar, with the rate vs. time dependence of degassing chosen to be similar to estimates of volcanic flux vs. time over this period.

The second of these models (Pepin 1994) included some thoughts on early evolution of volatile distribution on Mars. The EUV-powered hydrodynamic escape episode driving Ne-only loss from Earth, and loss of Kr and lighter gases from Venus, would have been intense enough on Mars to lift all the noble gases out of its primordial atmosphere. Early in this pre-3.7-Ga epoch, Xe isotopes were therefore assumed to have been hydrodynamically fractionated to their present composition, with corresponding depletions and fractionations of lighter primordial atmospheric constituents. Subsequent CO_2 pressure and isotopic history was dictated by the interplay of estimated losses to impact erosion, sputtering, and carbonate precipitation, additions by outgassing and carbonate recycling, and perhaps also by feedback stabilization under greenhouse conditions. In a subsequent model of the early Martian atmosphere, Carr (1999) examined the influences of these same mechanisms in controlling CO_2 pressure history, and was led to similar results and conclusions. It should be stressed, however, that since almost nothing is actually known about the values of the parameters governing these various processes, models of this epoch are no more than qualitative illustrations of how they might have driven early atmospheric behavior.

Pepin's (1994) treatment of post-3.7-Ga evolution of Martian CO_2 , N_2 , and the noble gases, although differing somewhat in detail from that of Jakosky et al. (1994) and extended to include the radiogenic isotopes ^{40}Ar and ^{129}Xe , generated results close to those derived by Jakosky et al. Both models assume that early and late evolutionary stages on Mars were separated by atmospheric CO_2 pressure collapse near 3.7 Ga. Sputtering loss of an atmospheric species relative to that of CO_2 is directly proportional to its exobase mixing ratio with CO_2 , and so sputtering fractionation of the atmospheric noble gas inventory is generally modest in a pre-3.7-Ga atmosphere dominated by CO_2 (Jakosky et al. 1994). Pressure collapse of the major atmospheric constituent abruptly increases the mixing ratios of pre-existing Ar, Ne and N_2 at the exobase, and since escape fluxes are proportional to exobase mixing ratios (see "Sputtering" section above), CO_2 collapse triggers their rapid removal by sputtering. This has the interesting consequence that no isotopic memory of their earlier processing survives. Current abundances and isotopic compositions are entirely determined by the action of sputtering and photochemical escape on gases supplied by outgassing during the late evolutionary epoch, and final distributions of the light noble gases and nitrogen are therefore decoupled from whatever their elemental and isotopic inventories might have been in the pre-3.7 Ga atmosphere. The present atmospheric Kr inventory (Fig. 6) also derives almost completely from solar-like Kr degassed during this period, which overwhelms the fractionated component inherited across the collapse episode—as noted above in the "Sputtering" section, both Kr and Xe are too massive to be sensibly affected by sputtering loss and fractionation during the late evolutionary stage. Consequently, among current observables, only the Xe isotopes and $\delta^{13}\text{C}$ survive as isotopic tracers of atmospheric history prior to its transition to low pressure. The assumption that early hydrodynamic escape fractionated the nonradiogenic Xe isotopes to at least approximately their present composition severely limits subsequent additions of unfractionated Xe to the atmospheric inventory by outgassing (consistent with the low degree of planetary degassing deduced above from radiogenic noble gas isotopes) or late-stage veneer accretion. This constraint, which threads through all hydrodynamic loss models for the terrestrial planets, is perhaps their most vulnerable characteristic (see *Outstanding Issues* section below).

Jakosky and Jones (1997) reviewed progress up to that time in understanding some of the aspects of Martian atmospheric evolution. There have been several developments since the work of Jakosky et al. (1994) and Pepin (1994). Hutchins and Jakosky (1996) revisited the late evolution sputtering-degassing models to investigate in more detail the parameters controlling the evolution of Ne and Ar abundances and isotopes (including radiogenic ^{40}Ar), in particular those relating to Martian degassing history. Their interesting conclusion was that the outgassing flux of Ar and Ne attributable to degassing during epochs of volcanic activity would have been ~ 1 -3 orders of magnitude too low to appropriately balance sputtering losses, and thus another major source of juvenile volatiles must have contributed to the atmosphere over geologic time, perhaps via input from gas-enriched hydrothermal systems. Hutchins et al. (1997) explored the important question of the extent to which a Martian paleomagnetic dipole field would have throttled sputtering losses by deflecting the solar wind around the upper atmosphere, and calculated the conditions, as functions of the time when paleomagnetic suppression of the sputtering mechanism ended, under which the combination of sputtering and degassing would still have generated present-day Ar and Ne distributions. The possible influence of an early global magnetic field on atmospheric evolution became more than a purely theoretical consideration with the discovery by Mars Global Surveyor of large-scale remnant magnetic lineations in the old Martian southern highlands (Connerney et al. 1999). The question of the existence of an active dynamo in Mars appears to be no longer if, but when.

Primordial xenon

Attempts to derive the compositions of the contemporary atmospheres on Earth and Mars from primitive nebular, planetesimal, or planetary source reservoirs have had to confront, in one way or another, an apparent decoupling of the evolutionary histories of Xe from those of Kr and the lighter noble gases. On Mars, for example, Xe is regarded as a highly fractionated residue of a likely CI- or solar-like progenitor composition; Kr, in contrast, appears to be unfractionated from an isotopically solar composition (Swindle 2002, this volume). This implies spatially and/or temporally separate provenances for these two species, processing mechanisms operating at different times, or both. In the models discussed in this section, atmospheric Xe inventories on both planets are considered to be fractionated relicts of their primary atmospheric Xe, while most of the Kr and lighter noble gases are products of planetary outgassing, compositionally modified on Mars by sputtering losses during the late evolutionary epoch.

Xenon therefore plays a crucial role in models of atmospheric evolution in which noble gases are fractionated from their initial compositions to isotopically heavier distributions by early hydrodynamic escape—it is the only observable among the noble gases that preserves a signature, albeit fractionated, of primordial atmospheric composition. With the assumption that nonradiogenic Xe isotope ratios in present-day atmospheres on Earth and Mars were generated in this way, backward modeling from these ratios through the fractionating process can in principle identify likely parental Xe compositions and thus the probable sources of noble gases in pre-escape atmospheres.

Current results of this exercise, using the Xe component compositions listed in Table 1, are reviewed in Pepin (2000). Applied to Earth, a modeling procedure involving derivation of fractionation relationships between nonradiogenic terrestrial and meteoritic Xe compositions simultaneously identifies a composition named U-Xe as primordial Xe, and establishes the presence of an atmospheric Xe component due principally to fission of extinct ^{244}Pu , as noted earlier in this chapter. Hydrodynamic escape of U-Xe leaves its fractionated residue on Earth. Evolution of atmospheric Xe from this early composition to its present isotopic state by subsequent degassing of fission and radiogenic

components from the crust and mantle is shown schematically in Figure 13. To fill in the deficits at isotopes ^{129}Xe and $^{131-136}\text{Xe}$, Pu-Xe must comprise $4.65 \pm 0.30\%$ of atmospheric ^{136}Xe , and $6.8 \pm 0.5\%$ of the present abundance of ^{129}Xe is from decay of extinct ^{129}I . (A more accurate re-calculation of U-Xe composition by Pepin (2000) is responsible for the increase in the Pu-Xe contribution from Pepin's (1997) estimate of 3.9%).

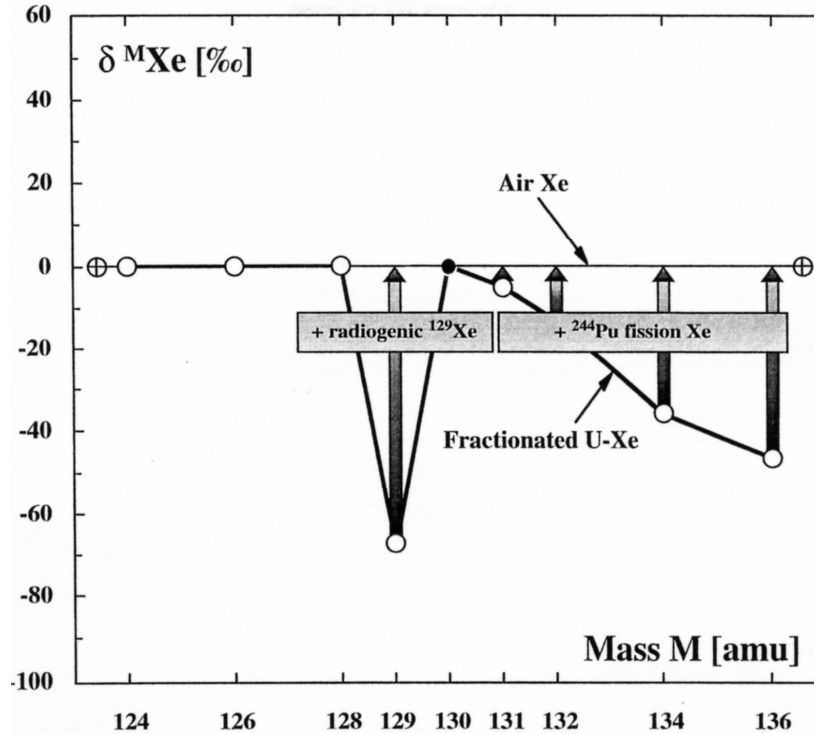


Figure 13. Post-escape evolution of Xe in the Earth's atmosphere (Pepin 2000). Escape-fractionated U-Xe defines an initially nonradiogenic terrestrial Xe composition (NEA-Xe, Table 1) to which radiogenic and fissionogenic components generated by decay of ^{129}I and ^{244}Pu in the crust and mantle were subsequently added by planetary outgassing.

The derived U-Xe composition is identical to that measured for solar-wind (SW) Xe except for relative underabundances of the two heaviest isotopes—an unexpected difference since the modeling otherwise points to solar wind compositions for the lighter noble gases in the primordial terrestrial atmosphere. However, as pointed out earlier (see Fig. 7 and associated discussion), SW-Xe cannot serve as primordial terrestrial Xe because its required fractionation generates a large overabundance of ^{136}Xe in the present atmosphere. Fractionated U-Xe ratios fall below the current atmosphere at $^{131-136}\text{Xe}$, defining a nonradiogenic terrestrial Xe spectrum to which a fissionogenic component is later added (Fig. 13); this property of the U-Xe composition is intrinsic to its derivation.

In contrast to Earth, Martian Xe apparently did not evolve from a U-Xe progenitor. Modeling derivation of primordial Xe composition on Mars is based on analyses of atmospheric gases trapped in glassy phases of SNC meteorites (Swindle 2002, this volume). Present ambiguities in this data base are such that two different solar-system Xe compositions, carbonaceous chondrite (CI)-Xe and SW-Xe, are possible candidates—but not U-Xe. Exclusion of U-Xe as the dominant primordial atmospheric inventory on Mars, despite the implication of the terrestrial modeling that it was a major component of the nebular gas phase, requires that accretion of CI- or SW-Xe-rich materials from sources more localized in space or time has overwhelmed the isotopic signature of its presence.

Swindle et al. (1986) pointed out that nonradiogenic Xe trapped in the glassy lithology of the SNC meteorite EET79001 strongly resembles mass-fractionated CI-Xe. Pepin (1991, 1994) chose CI-Xe to represent the primordial Xe composition on Mars in modeling the isotopic evolution of its atmosphere, in part based on Swindle et al.'s observation but also because, as noted earlier, a meteoritic source is consistent with models of the bulk chemical composition of the planet. The fact that fractionated CI-Xe *by itself* provides an excellent match to the Mars atmospheric composition, in particular at the four heaviest isotopes, has the interesting and somewhat unsettling consequence that additional contributions to the Xe inventory from degassed fission Xe are either very minor or absent altogether. And yet the present atmosphere is clearly heavily enriched in ^{129}Xe from extinct ^{129}I decay (Swindle 2002). The presence of radiogenic ^{129}Xe but apparently little if any ^{244}Pu -fission Xe, a situation quite unlike that on Earth, has been awkward to reconcile with models of Martian geochemical evolution and degassing history. Swindle and Jones (1997) considered this problem in detail, and constructed an alternative model of atmospheric evolution on Mars—using an atmospheric Xe composition close to that measured by Swindle et al. (1986)—with the specific objective of accommodating, if possible, a Pu fission Xe component. They chose SW-Xe rather than CI-Xe as primordial Xe, and demonstrated that an appropriate fractionation of this composition fell below measured Martian atmospheric $^{131-136}\text{Xe}/^{130}\text{Xe}$ ratios by amounts completely consistent within error with the presence of an additional component with Pu-Xe fission yield ratios; moreover the calculated fissiogenic ^{136}Xe abundance was $\sim 5\%$ of total ^{136}Xe , similar to the fraction derived above for Earth.

Mathew et al. (1998) revised the earlier data base for Martian atmospheric Xe by including measurements of Xe composition in the Zagami shergotite and recalculating corrections for spallation Xe produced during the space exposures of SNC meteorites to cosmic-ray irradiation. The average of the data sets they judged to be of highest quality, plotted in Figure 14 referenced to SW-Xe, differs from Swindle et al.'s (1986) composition by $<10\%$ except for a $\sim 60\%$ decrease in $\delta^{124}\text{Xe}$; their data are seen in the figure to be almost perfectly fit by hydrodynamic escape fractionation of SW-Xe, and thus could be consistent with no ^{244}Pu fission Xe contribution at all. However the second curve in Figure 14, which represents a somewhat less fractionated SW-Xe composition along the lines suggested by Swindle and Jones (1997), yields heavy-isotope residuals in excellent accord with addition of a Pu-Xe component at close to the 5% level at ^{136}Xe , although agreement with Mathew et al.'s (1998) light isotope ratios is somewhat degraded. Other than the criterion of quality of fit to measured isotopic distributions, there is nothing in the modeling of Martian Xe evolution by hydrodynamic escape that points to one or the other of these two fractionations as preferable.

It is important to note that if we return to the earlier assumption that CI-Xe represents the Martian primordial composition and renormalize Mathew et al.'s (1998) atmospheric ratios to CI-Xe, fractionated CI-Xe is found to be a significantly poorer fit to the data, particularly at the three lightest isotopes. The fractionation curve that best matches these light isotope ratios passes well above the heavy isotope data field, thus excluding CI-Xe as a candidate for primordial Martian Xe if the Mathew et al. composition really represents Mars. On the other hand, the original Swindle et al. (1986) data are compatible within error with fractionated CI-Xe at all isotopes. Until we know the actual Xe composition on Mars more precisely, either possibility is arguably viable. The key discriminators in ruling between these two primordial Xe candidates—and between the two curves in Figure 14, one of which allows a Pu-Xe component and the other not—are clearly the light isotope ratios, unfortunately both the most difficult to measure and the most subject to spallogenic perturbations.

The composition of primordial Xe on Mars and the presence or absence of ^{244}Pu fission Xe in the present atmosphere are important issues in the context of the provenance of accretional materials, the timing of planetary growth, and the subsequent geochemical and outgassing histories of the planet (e.g., see the earlier discussion of the Martian fissiogenic Xe budget). At the moment, the central question of the presence or absence of Pu-Xe is plagued by apparent coincidences. The excellent match of fractionated SW-Xe alone to the atmospheric data in Figure 14 is presumably fortuitous if Pu-Xe is present; and if it is absent, the fact that a weaker fractionation generates heavy-isotope residuals in good accord with ^{244}Pu fission yields must likewise be accidental.

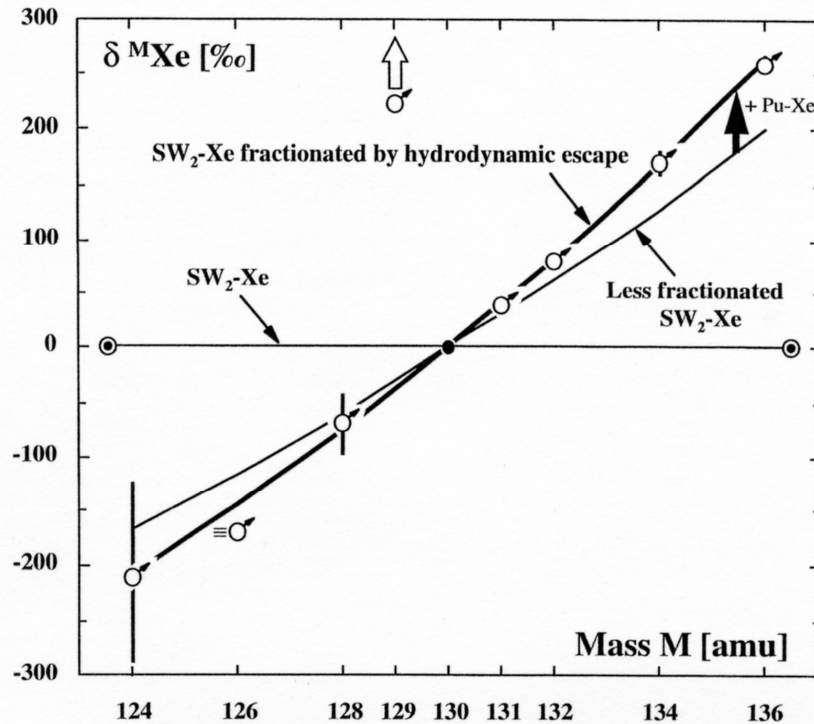


Figure 14. Mathew et al.'s (1998) Martian atmospheric composition plotted relative to $\text{SW}_2\text{-Xe}$ (data from Table 1). The heavy curve demonstrates that $\text{SW}_2\text{-Xe}$ in the primordial Martian atmosphere can be fractionated by escape to a close fit to all atmospheric isotope ratios except $\delta^{129}\text{Xe}$ (off-scale at +1480‰). The light curve represents a less severely fractionated $\text{SW}_2\text{-Xe}$ composition which allows an additional component, isotopically consistent with $^{244}\text{Pu-Xe}$ at $M = 131\text{-}136$, in the present atmosphere (as suggested by Swindle and Jones 1997), but at the expense of a poorer fit to the nominal values of Mathew et al.'s (1998) light isotope ratios.

There remains the question of how and when Mars might have acquired solar wind-like Xe if that was indeed the primordial planetary composition. One possibility is that its accretional feedstock was ancient enough to have trapped ambient nebular gases during the early sun-building stage of disk evolution—thus sampling the same Xe that now comprises the solar inventory—and somehow eluded being swept into the sun. In this view Mars is an “older” planet than Earth. Alternatively, perhaps it is “younger” in the sense that a significant fraction of its pre-accretional materials were exposed, after formation of the Earth, to direct solar-wind irradiation in a waning dusty nebula which was thin enough to permit wind penetration to planetary distances but still opaque enough through the midplane to attenuate the solar EUV radiation that later powered hydrodynamic escape of Mars’ primordial atmosphere.

OUTSTANDING ISSUES

Some progress has been made in the long-standing problem of understanding the sources of volatiles on and in the terrestrial planets, and the processes that could plausibly have driven their initial atmospheres down planet-specific evolutionary tracks to the amazingly divergent compositional states we observe today on Earth, Mars and Venus. Some of the ideas and models described in this chapter, although perhaps conceptually attractive, will turn out to be irrelevant in the sense that nature chose different paths. Others could be headed in the right direction but lack the data needed for meaningful experimental and observational tests of their predictive power. In this respect it is likely that much of our sharpening of volatile origin and evolution issues will emerge, at least in the near term, from studies of the terrestrial atmosphere-interior system where the data base is relatively large and growing, especially for volatile distributions in the Earth's mantle. Further progress toward the ultimate objective of understanding all three of the terrestrial planets as a linked class of objects clearly hinges on how much more we can learn about volatile abundances and compositions of noble gases and other atmophilic species on Venus and Mars. Venus, at the moment, is characterized only by the immensely valuable but still incomplete and relatively imprecise reconnaissance data from the Pioneer Venus and Venera spacecraft missions of the late 1970s. The combination of Viking in-situ measurements and the happy advent of the SNC meteorites has given us a much more quantitative view of the present state and possible history of Martian volatiles. Current modeling, however, is pushing beyond the edge of what is actually known about Mars, and now requires data constraints at levels of precision probably attainable only by laboratory analyses—in particular, in the context of this chapter, of a returned atmospheric sample. For Venus, on the other hand, the uncertainties noted in the modeling discussion—including the central issue of whether Venusian Xe does or does not resemble U-Xe—could be addressed, at least to first order, by in-situ measurements at precisions within the capabilities of current spacecraft instrumentation.

In this concluding section we summarize our views of the status of some of the current efforts to decipher volatile evolutionary history. This is by no means a comprehensive overview of the field. It concentrates instead on areas that appear to the authors to have the greatest potential for illuminating the general problem.

Acquisition of noble gases by planetary interiors. The evidence for primordial noble gases trapped deep within the Earth with solar (implanted or captured) Ne isotope characteristics, is unambiguous. Supplying these volatiles into the growing Earth will likely be related to the processes generating the initial atmosphere, although further surface additions may be possible. The capture of a primordial atmosphere by gravitational attraction of nebular gas is inescapable if the growing planet reaches sufficient mass in the presence of the nebula, and so the first criteria for this mechanism is firmly establishing if such a nebular history occurred. How much gas was then trapped in the Earth is a more complex issue requiring a substantial modeling effort. Parameters that need further consideration include the structure of the atmosphere, how long will the underlying mantle be molten and to what depth, and how this process is affected by continuing accretion. Whether or not this supplies deep mantle noble gases, a shallower reservoir may be more readily created that has supplied noble gases to the atmosphere and may no longer be represented in the mantle. Under conditions in which melting of the underlying planet is not achieved, adsorption of noble gases, enhanced by the increased pressure of the gravitationally focused nebular gases, may be an important source of noble gases that may become buried during accretion. Overall, it appears that there are various ways in which gravitational attraction of nebula gases can lead to

acquisition of both atmospheric and interior noble gases, and the specific mechanisms that dominated depend upon the extent of aggregation by the time of nebula dispersal, and the temperature/pressure histories of the protoplanetesimals.

Burial of material bearing solar noble gases implanted by radiation also remains an option for the source of mantle noble gases. This requires the opposite conditions of gravitational capture; clearance of the solar nebula prior to substantial aggregation of solids to allow penetration of solar wind to where the terrestrial planets accumulate. However large protoplanetary objects, carrying irradiated regolith materials that comprise small fractions of their total masses, will be inefficient in supplying solar wind gases to planets, and may have already acquired noble gas budgets dominated by gravitational capture mechanisms. Here again, the history of the solar nebula is the deciding factor. One important constraint may come from resolving whether the mantle contains Ne with the isotopic composition of the solar nebula, rather than of implanted Ne-B.

Atmospheric origin and evolution. Hydrodynamic escape models, with appropriate numerical choices for free parameters and of primordial atmospheric and planetary interior compositions, are capable of replicating details of contemporary isotopic distributions as subtle as the need to degas nucleogenic ^{21}Ne from the terrestrial crust in an amount close to that predicted by independent calculations. One should recognize, however, that the model is highly parameterized and intrinsically multi-stage, requiring both escape fractionation and subsequent mixing with species degassed from planetary interiors in specific elemental proportions to generate contemporary elemental and isotopic abundances (e.g., Fig. 11). As promising as the modeling results may appear, they nevertheless should not obscure the fact that this evolutionary sequencing, and the parameter values controlling it, are subject to important uncertainties of one kind or another. For example, it seems clear that some degree of hydrodynamic loss and fractionation of planetary atmospheres would have been inevitable if the required conditions for energy source, hydrogen supply, and, in the case of solar EUV-driven escape, midplane transparency were even partially met. But the question of what species would actually be lost is another matter. The simple analytic theory outlined in this chapter assumes a hydrogen-dominated atmosphere and energy-limited escape, both arguably reasonable suppositions of primordial atmospheric conditions. However such atmospheres might also have contained substantial amounts of a heavy constituent, say CO_2 , and in this case the escape flux of H_2 would have been limited by its ability to diffuse through the CO_2 . Zahnle et al. (1990a) and Ozima and Zahnle (1993) have shown that only Ne and some Ar would be hydrodynamically lost under these conditions, with obvious implications for the possibility of Xe fractionation by this mechanism. A more complete short-term atmospheric blowoff, including heavier species, could have been driven by a very large deposition of collisional energy, but as noted above it has not been demonstrated that post-giant impact conditions would have led naturally to generation of large isotopic fractionations by hydrodynamic escape. Nor can one convincingly defend the implicit assumption that Venus' atmosphere was not also altered to some unknown degree by large-scale impact. Note also that the extents of Xe fractionation from primordial to present composition are similar on both Earth and Mars despite the much smaller mass of Mars, the apparent differences —U-Xe versus solar wind Xe— in their sources of precursor Xe, the much greater overall depletion of Martian noble gases, and the possibility that escape episodes were powered by distinctly different energy sources —EUV radiation on Mars versus giant impact on Earth. Is this just coincidence, or the expression of some more fundamental fractionating process that left similar signatures on all three of the terrestrial planet atmospheres?

Atmospheric Xe inventories in hydrodynamic escape modeling are considered to be

fractionated relicts of their primary atmospheric Xe, while most of the Kr and lighter noble gases are products of planetary outgassing. This effective decoupling of the heaviest noble gas from lighter species follows naturally from the processes intrinsic to the model, in all respects but one. Isotope mixing systematics impose strict upper limits on the allowed levels of “contamination” of residual primary Xe by later addition of isotopically unfractionated Xe degassed from the interior or supplied by subsequent accretion of noble gas carrier materials, a constraint that applies with equal force to the model in which pre-fractionated Xe is delivered to planets by porous planetesimals. Estimates of these limits for Earth and Mars (Pepin 1991, 1994) fall well below the amounts of Xe that ordinarily would be expected to accompany the outgassed Kr components, and so one of two possible assumptions must be made about the Xe initially present in their interior reservoirs. Either it was largely sequestered within the planets by some mechanism and thus was never substantially transported to the atmosphere, or, following the fractional degassing models of Zhang and Zindler (1989) and Tolstikhin and O’Nions (1994), Xe was preferentially outgassed well before the bulk of the lighter noble gases, and most of it was already present in the primary atmospheres prior to Xe-fractionating hydrodynamic loss. Pepin (1991) originally proposed Xe retention deep in the planet by preferential partitioning into solid iron phases under high pressure. However Caldwell et al. (1997) have since shown experimentally that Xe does not alloy with iron even at pressures as high as that at the terrestrial core-mantle boundary. Jephcoat (1998) suggested an alternative sequestering process in which Xe atoms condense into initially nanometer-size solids in the deep mantle and segregate toward the core, although here the question arises as to whether separated phases of an element of such low abundance would be likely to form.

Whatever the mechanism, models that appeal to early fractionation of Xe from primordial to present-day planetary compositions, by hydrodynamic escape or in porous pre-planetary planetesimals, are viable only to the extent that the ancient fractionated Xe signatures can be preserved against major compositional perturbation by later additions of degassed or accreted noble gas components carrying isotopically different Xe. That this kind of isotopic pollution has not occurred is one of the more crucial assumptions of the modeling. In this context, it is clear that a version of the classical “missing Xe” problem is still with us—no longer driven, as it was originally, by the strikingly lower Xe/Kr elemental ratio in the terrestrial atmosphere compared to the chondritic meteorites, but now, in escape modeling, centered on the Xe isotopes and the postulated deficit in Xe degassed from planetary interiors.

The importance of Venus. High noble gas abundances and, within their substantial uncertainties, solar-like elemental ratios (except for Ne/Ar) suggest that at least the heavier noble gases on Venus are not greatly evolved from their primordial states (Cameron 1983; Pepin 1991). Neon and Ar isotope ratios also appear to be displaced toward solar values compared to their terrestrial counterparts. Venus therefore occupies a unique position among the triad of terrestrial planets in that its atmosphere may have been altered from its initial compositional configuration by planet-specific fractionating loss mechanisms to a much smaller extent than the highly processed atmospheres on Earth and Mars.

If this is the case, atmospheric compositions on Venus are enormously important in the context of models for the origin and evolution of terrestrial planet volatiles, particular in the case of Xe. The general similarity of nonradiogenic Xe isotope ratios on Earth and Mars is the strongest argument in favor of the fractionation of Xe on common pre-planetary carriers rather than on the planets themselves, although the correspondence does not appear to be exact. The ability of Venusian Xe to rule between the predictions of

this and the hydrodynamic escape model was pointed out previously. Moreover, if Xe on Venus turns out to be isotopically lighter than terrestrial Xe, the extent to which it differs from solar composition could discriminate between hydrodynamic escape driven on all three planets entirely by intense solar EUV radiation, which would result in loss and fractionation of Venusian Xe (Pepin 1991), and a hybrid giant impact—EUV energy supply on Earth, which would not.

An equally significant question is whether nonradiogenic Xe on Venus, if solar-like, is compositionally closer to SW-Xe or to U-Xe, or to modestly fractionated derivatives of one or the other. One might expect that Earth and its sister planet would both have acquired their primordial gases from similar source(s) at about the same time, and that the U-Xe required for Earth in the modeling would also have been present in Venus' early atmosphere. If it was, the mystery of Mars' apparently different primordial Xe composition—SW-Xe or perhaps CI-Xe—is deepened; but if Venusian Xe more closely resembles SW-Xe, then Earth is the modeling anomaly.

The issue of what the composition of nebular gases actually was at the time(s) of planetary formation is clearly a central one for models which propose direct (gravitational condensation) or indirect (cometary carriers) nebular sources of primordial planetary volatiles. The solar wind has been adopted as a proxy of early nebular composition throughout the modeling discussed above, with the obvious exception of U-Xe. Xenon in Jupiter's atmosphere is of great importance in this context since it is one step closer to representing the ancient nebula than the solar wind, where the possibility of isotopic fractionation in processes transporting and releasing bulk solar Xe to and from the corona cannot be completely disregarded. Results from the Galileo Probe mass spectrometer (Table 1; Mahaffy et al. 2000) have narrowed the range of possible nebular Xe compositions at the time of Jovian atmospheric formation. Data scatter is substantial,

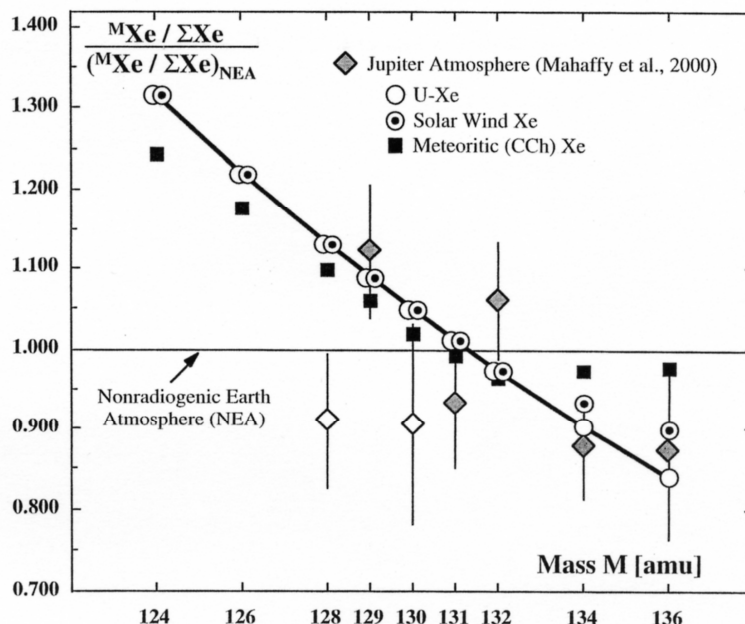


Figure 15. Jupiter atmospheric Xe composition measured by the Galileo Probe mass spectrometer (Mahaffy et al. 2000), calculated as the abundance of each isotope M divided by the total abundance for all M and plotted relative to the NEA-Xe composition (Table 1) represented in the same way. The five most abundant Jovian Xe isotopes are indicated by the shaded symbols. U-Xe, SW₂-Xe, and AVCC-Xe compositions in Table 1 are shown for comparison in the same representation. The data indicate deficits at the two heaviest isotopes relative to NEA-Xe and AVCC-Xe, but uncertainties are too large to rule between SW-Xe and U-Xe as the Jovian composition.

as seen in Figure 15, but relative abundances of the most abundant isotopes (^{129}Xe and $^{131-136}\text{Xe}$) fall approximately along a fractionation curve with respect to nonradiogenic terrestrial Xe. The best-fit fractionation is most consistent with U-Xe at $^{134-136}\text{Xe}$ although SW-Xe is allowed within 1σ uncertainties. The major-isotope pattern is incompatible with terrestrial Xe, suggesting that cometary ices acquiring their noble gases from the early nebula did not deliver Earth's present-day Xe composition to the planet.

Coupled histories of atmospheric and interior planetary volatiles. Highly detailed models of noble gas sources and evolution have been developed separately and almost independently for the atmosphere and interior of the Earth (e.g., Pepin 1991, 1997, 2000; Porcelli and Wasserburg 1995a,b,c; see Porcelli and Ballentine 2002). But the origin and history of atmospheric noble gases are not independent of the sources, distributions, and transport histories of noble gases within a planet—these two volatile systems must clearly be linked in nature through their primordial inventories and the processes of degassing and subduction. Indeed, many models of the atmosphere require degassing of some portion of the planetary interior, and mantle models include degassing of the atmosphere. The question, so far largely unexplored, is whether the requirements implicit in each of these models for the dynamical and compositional history of the other reservoir are compatible, and, if not, what the inconsistencies are and how might they be addressed. Integration of these historically separate approaches into a single consistent view of coupled volatile evolution in planetary atmospheres and interiors would be a major advance in the modeling research described in this chapter.

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REFERENCES

- Abe Y, Matsui T (1986) Early evolution of the Earth: accretion, atmosphere formation and thermal history. Proc 17th Lunar Planet Sci Conf, J Geophys Res 91:E291-E302
- Ahrens TJ (1990) Earth accretion. In Origin of the Earth. Newsom HE, Jones JH (eds), Oxford University Press, New York, p 211-227
- Ahrens TJ (1993) Impact erosion of terrestrial planetary atmospheres. Ann Rev Earth Planet Sci 21: 525-555
- Ahrens TJ, O'Keefe JD, Lange MA (1989) Formation of atmospheres during accretion of the terrestrial planets. In Origin and Evolution of Planetary and Satellite Atmospheres. Atreya SK, Pollack JB, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 328-385
- Albarède (1998) Time-dependent models of U-Th-He and K-Ar evolution and the layering of mantle convection. Chem Geol 145:413-429
- Allègre CJ, Staudacher T, Sarda P, Kurz M (1983) Constraints on evolution of Earth's mantle from rare gas systematics. Nature 303:762-766
- Allègre CJ, Staudacher T, Sarda P (1986) Rare gas systematics: formation of the atmosphere, evolution and structure of the Earth's mantle. Earth Planet Sci Lett 81: 127-150
- Allègre CJ, Hofmann A, O'Nions RK (1996) The argon constraints on mantle structure. Geophys Res Lett 23:3555-3557
- Anders E, Grevesse N (1989) solar-system abundances of the elements. Geochim Cosmochim Acta 53: 197-214
- Anderson DL (1998a) The helium paradoxes. Proc Natl Acad Sci USA 95:4822-4827
- Ayres TR (1997) Evolution of the solar ionizing flux. J Geophys Res 102:1641-1651
- Ballentine CJ, Burnard PG (2002) Production and release of noble gases in the continental crust. Rev Mineral Geochem 47:481-538
- Ballentine CJ, Porcelli D, Wieler R (2001) Technical comment on 'Noble gases in mantle plumes' by Trieloff et al. (2000). Science 291:2269a
- Bar-Nun A, Herman G, Laufer D, Rappaport ML (1985) Trapping and release of gases by water ice and implications for icy bodies. Icarus 63:317-332

- Basford JR, Dragon JC, Pepin RO, Coscio MR Jr, Murthy VR (1973) Krypton and xenon in lunar fines. *Proc Lunar Sci Conf 4th*, p 1915-1955
- Begemann F, Weber HW, Hintenberger H (1976) On the primordial abundance of argon-40. *Astrophys J* 203:L155-L157
- Benz W, Cameron AGW (1990) Terrestrial effects of the giant impact. *In* *Origin of the Earth*. Newsom HE, Jones JH (eds) Oxford University Press, New York, p 61-67
- Bernatowicz TJ, Kennedy BM, Podosek FA (1985) Xe in glacial ice and the atmospheric inventory of noble gases. *Geochim Cosmochim Acta* 49:2561-2564
- Bernatowicz TJ, Podosek FA (1986) Adsorption and isotopic fractionation of Xe. *Geochim Cosmochim Acta* 50:1503-1507
- Bernatowicz TJ, Podosek FA, Honda M, Kramer FE (1984) The atmospheric inventory of xenon and noble gases in shales: The plastic bag experiment. *J Geophys Res* 89:4597-4611
- Bogard DD (1997) A reappraisal of the Martian Ar-36/Ar-38 ratio. *J Geophys Res* 102:1653-1661
- Bogard DD, Clayton RN, Marti K, Owen T, Turner G (2001) Martian volatiles: isotopic composition, origin, and evolution. *Space Sci Rev* 96:425-458
- Brown H (1949) Rare gases and formation of the earth's atmosphere. *In* *The Atmospheres of the Earth and Planets*. Kuiper GP (ed), University of Chicago Press, Chicago, p 258-266
- Busemann H, Baur H, Wieler R (2000) Primordial noble gases in "phase Q" in carbonaceous and ordinary chondrites studied by closed-system stepped etching. *Meteorit Planet Sci* 35:949-973
- Caffee MW, Hudson GU, Velsko C, Huss GR, Alexander Jr EC, Chivas AR (1999) Primordial noble gases from Earth's mantle: identification of a primitive volatile component. *Science* 285:2115-2118
- Caldwell WA, Nguyen JH, Pfrommer BG, Mauri F, Louie SG, Jeanloz R (1997) Structure, bonding, and geochemistry of xenon at high pressures. *Science* 227:930-933
- Cameron AGW (1983) Origin of the atmospheres of the terrestrial planets. *Icarus* 56:195-201
- Cameron AGW, Ward WR (1976) The origin of the Moon. *Lunar Science VII*, Lunar and Planetary Institute, Houston, p 120-122
- Canalas R, Alexander EC Jr, Manuel OK (1968) Terrestrial abundance of noble gases. *J Geophys Res* 73:3331-3334
- Carr MH (1999) Retention of an atmosphere on early Mars. *J Geophys Res* 104:21897-21909
- Carroll MR, Stolper EM (1993) Noble gas solubilities in silicate melts and glasses: new experimental results for argon and the relationship between solubility and ionic porosity. *Geochim Cosmochim Acta* 57:5039-5051
- Chen GQ, Ahrens TJ (1997) Erosion of terrestrial planet atmosphere by surface motion after a large impact. *Phys Earth Planet Int* 100:21-26
- Chyba CF (1990) Impact delivery and erosion of planetary oceans in the early inner solar system. *Nature* 343:129-133
- Chyba CF (1991) Terrestrial mantle siderophiles and the lunar impact record. *Icarus* 92:217-235
- Clarke WB, Bet MA, Craig H (1969) Excess ³He in the sea: evidence for terrestrial primordial helium. *Earth Planet Sci Lett* 6:213-220
- Connerney JEP, Acuña MH, Wasilewski PJ, Ness NF, Rème H, Mazelle C, Vignes D, Lin RP, Mitchell DL, Cloutier PA (1999) Magnetic lineations in the ancient crust of Mars. *Science* 284:794-798
- Donahue TM (1986) Fractionation of noble gases by thermal escape from accreting planetesimals. *Icarus* 66:195-210
- Donahue TM, Pollack JB (1983) Origin and evolution of the atmosphere of Venus. *In* *Venus*. Hunten D, Colin L, Donahue T, Moroz V (eds) University of Arizona Press, Tucson, Arizona, p 1003-1036
- Donahue TM, Russell CT (1997) The Venus atmosphere and ionosphere and their interaction with the solar wind: an overview. *In* *Venus II*. Bougher SW, Hunten DM, Phillips RJ (eds) University of Arizona Press, Tucson, Arizona, p 3-31
- Donahue TM, Hoffman JH, Hodges RR Jr (1981) Krypton and xenon in the atmosphere of Venus. *Geophys Res Lett* 8:513-516
- Dreibus G, Wänke H (1985) Mars, a volatile-rich planet. *Meteoritics* 20:367-381
- Dreibus G, Wänke H (1987) Volatiles on Earth and Mars: A comparison. *Icarus* 71:225-240
- Dreibus G, Wänke H (1989) Supply and loss of volatile constituents during the accretion of terrestrial planets. *In* *Origin and Evolution of Planetary and Satellite Atmospheres*. Atreya SK, Pollack JB, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 268-288
- Eugster O, Eberhardt P, Geiss J (1967) The isotopic composition of krypton in unequilibrated and gas-rich chondrites. *Earth Planet Sci Lett* 2: 385-393
- Fanale FP, Cannon WA (1971) Physical adsorption of rare gas on terrigenous sediments. *Earth Planet Sci Lett* 11:362-368
- Fanale FP, Cannon WA (1972) Origin of planetary primordial rare gas: The possible role of adsorption. *Geochim Cosmochim Acta* 36:319-328

- Feigelson ED, Kriss GA (1989) Soft X-ray observations of pre-main-sequence stars in the Chamaeleon dark cloud. *Astrophys J* 338:262-276
- Frick U, Mack R, Chang S (1979) Noble gas trapping and fractionation during synthesis of carbonaceous matter. *Proc 10th Lunar Planet Sci Conf*, p 1961-1973
- Frick U, Becker RH, Pepin RO (1988) Solar wind record in the lunar regolith: Nitrogen and noble gases. *Proc 18th Lunar Planet Sci Conf*, p 87-120
- Garrison DH, Bogard DD (1998) Isotopic composition of trapped and cosmogenic noble gases in several Martian meteorites. *Meteorit Planet Sci* 33:721-736
- Gierasch PJ, Toon OB (1973) Atmospheric pressure variation and the climate of Mars. *J Atmos Sci* 30:1502-1508
- Graham DW, Lupton F, Albarède F, Condomines M (1990) Extreme temporal homogeneity of helium isotopes at Piton de la Fournaise, Réunion Island. *Nature* 347:545-548
- Graham DW (2002) Noble gases in MORB and OIB: observational constraints for the characterization of mantle source reservoirs. *Rev Mineral Geochem* 47:247-318
- Graham DW, Lupton F, Albarède F, Condomines M (1990) Extreme temporal homogeneity of helium isotopes at Piton de la Fournaise, Réunion Island. *Nature* 347:545-548
- Haberle RM, Tyler D, McKay CP, Davis WL (1992) Evolution of Mars' atmosphere: Where has the CO₂ gone? *Bull Am Astron Soc* 24:1015-1016
- Haberle RM, Tyler D, McKay CP, Davis WL (1994) A model for the evolution of CO₂ on Mars. *Icarus* 109:102-120
- Hanyu T, Kaneoka I (1998) Open system behavior of helium in case of the HIMU source area. *Geophys Res Lett* 25:687-690
- Harrison D, Burnard P, Turner G (1999) Noble gas behaviour and composition in the mantle: Constraints from the Iceland Plume. *Earth Planet Sci Lett* 171:199-207
- Hartmann WK, Davis DR (1975) Satellite-sized planetesimals and lunar origin. *Icarus* 24:504-515
- Hayashi C, Nakazawa K, Mizuno H (1979) Earth's melting due to the blanketing effect of the primordial dense atmosphere. *Earth Planet Sci Lett* 43:22-28
- Helffrich GR, Wood BJ (2001) The Earth's mantle. *Nature* 412:501-507
- Hilton DR, Grönvold K, MacPherson CG, Castillo PR (1999) Extreme ³He/⁴He ratios in northwest Iceland: constraining the common component in mantle plumes. *Earth Planet Sci Lett* 173:53-60
- Hiyagon H, Ozima M, Marty B, Zashu S, Sakai H (1992) Noble gases in submarine glasses from mid-oceanic ridges and Loihi Seamount: constraints on the early history of the Earth. *Geochim Cosmochim Acta* 56:1301-1316
- Hoffman JH, Hodges RR, Donahue TM, McElroy MB (1980) Composition of the Venus lower atmosphere from the Pioneer Venus mass spectrometer. *J Geophys Res* 85:7882-7890
- Hohenberg CM, Podosek FA, Reynolds JH (1967) Xenon-iodine dating: sharp isochronism in chondrites. *Science* 156:233-236
- Honda M, McDougall I (1998) Primordial helium and neon in the Earth- a speculation on early degassing. *Geophys Res Lett* 25:1951-1954
- Honda M, McDougall I, Patterson DB, Dougeris A, Clague DA (1993) Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii—a solar component in the Earth. *Geochim Cosmochim Acta* 57:859-874
- Hudson GB, Kennedy BM, Podosek FA, Hohenberg CM (1989) The early solar system abundance of ²⁴⁴Pu as inferred from the St. Severin chondrite. *Proc 19th Lunar Planet Sci Conf*, p 547-557
- Hunten DM (1979) Capture of Phobos and Deimos by protoatmospheric drag. *Icarus* 37:113-123
- Hunten DM, Pepin RO, Walker JCG (1987) Mass fractionation in hydrodynamic escape. *Icarus* 69:532-549
- Hunten DM, Pepin RO, Owen TC (1988) Planetary Atmospheres. *In* Meteorites and the Early Solar System. Kerridge JF, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 565-591
- Hunten DM, Donahue TM, Walker JCG, Kasting JF (1989) Escape of atmospheres and loss of water. *In* Origin and Evolution of Planetary and Satellite Atmospheres. Atreya SK, Pollack JB, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 386-422
- Hutchins KS, Jakosky BM (1996) Evolution of martian atmospheric argon: Implications for sources of volatiles. *J Geophys Res* 101:14933-14949
- Hutchins KS, Jakosky BM, Luhmann JG (1997) Impact of a paleomagnetic field on sputtering loss of martian atmospheric argon and neon. *J Geophys Res* 102:9183-9189
- Igarashi G (1995) Primitive Xe in the Earth. *In* Volatiles in the Earth and Solar System. Farley KA (ed), Am Inst Phys Conf Proc 341:70-80
- Jakosky BM, Jones JH (1997) The history of martian volatiles. *Rev Geophys* 35:1-16
- Jakosky BM, Pepin RO, Johnson RE, Fox JL (1994) Mars atmospheric loss and isotopic fractionation by solar-wind-induced sputtering and photochemical escape. *Icarus* 111:271-288

- Jephcoat AP (1998) Rare-gas solids in the Earth's deep interior. *Nature* 393:355-358
- Kaula WM (1999) Constraints on Venus evolution from radiogenic argon. *Icarus* 139:32-39
- Krummenacher D, Merrihue CM, Pepin RO, Reynolds JH (1962) Meteoritic krypton and barium versus the general isotopic anomalies in xenon. *Geochim Cosmochim Acta* 26:231-249
- Kunz J (1999) Is there solar argon in the Earth's mantle? *Nature* 399:649-650
- Kunz J, Staudacher T, Allègre CJ (1998) Plutonium-fission xenon found in Earth's mantle. *Science* 280:877-880
- Kurz MD, Jenkins WJ, Hart SR (1982) Helium isotopic systematics of oceanic islands and mantle heterogeneity. *Nature* 297:43-46
- Laufer D, Notesco G, Bar-Nun A (1999) From the interstellar medium to Earth's oceans via comets—An isotopic study of HDO/H₂O. *Icarus* 140:446-450
- Lee D-C, Halliday AN, Snyder GA, Taylor LA (1997) Age and origin of the moon. *Science* 278:1098-1103
- Lewis JS, Prinn RG (1984) *Planets and their Atmospheres: Origin and Evolution*. Academic Press, Orlando, Florida
- Luhmann JG, Johnson RE, Zhang MHG (1992) Evolutionary impact of sputtering of the martian atmosphere by O⁺ pickup ions. *Geophys Res Lett* 19:2151-2154
- Lunine JI, Stevenson DJ (1985) Thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. *Astrophys J Suppl Series* 58:493-531
- Lux G (1987) The behavior of noble gases in silicate liquids: Solution, diffusion, bubbles and surface effects, with applications to natural samples. *Geochim Cosmochim Acta* 51:1549-1560
- Mahaffy PR, Donahue TM, Atreya SK, Owen TC, Niemann HB (1998) Galileo probe measurements of D/H and ³He/⁴He in Jupiter's atmosphere. *Space Sci Rev* 84:251-263
- Mahaffy PR, Niemann HB, Alpert A, Atreya SK, Demick J, Donahue TM, Harpold DN, Owen TC (2000) Noble gas abundance and isotope ratios in the atmosphere of Jupiter from the Galileo probe mass spectrometer. *J Geophys Res* 105:15061-15071
- Mamyrin BA, Tolstikhin IN, Anufriev GS, Kamenskiy IL (1969) Anomalous isotopic composition of helium in volcanic gases. *Dokl Adad Nauk SSR* 184:1197-1199 (in Russian)
- Marti K (1967) Isotopic composition of trapped krypton and xenon in chondrites. *Earth Planet Sci Lett* 3:243-248
- Marty B, Marti K (2002) Signatures of early differentiation on Mars. *Earth Planet Sci Lett* 196:251-263
- Mason EA, Marrero TR (1970) The diffusion of atoms and molecules. *Advan At Mol Phys* 6:155-232
- Mathew KJ, Marti K (2001) Early evolution of Martian volatiles: Nitrogen and noble gas components in ALH84001 and Chassigny. *J Geophys Res* 106:1401-1422
- Mathew KJ, Marti K (2002) Martian atmospheric and interior volatiles in the meteorite Nakhla. *Earth Planet Sci Lett* 199:7-20
- Mathew KJ, Kim JS, Marti K (1998) Martian atmospheric and indigenous components of xenon and nitrogen in the Shergotty, Nakhla, and Chassigny group meteorites. *Meteorit Planet Sci* 33:655-664
- Matsuda J, Matsubara K (1989) Noble gases in silica and their implication for the terrestrial "missing" Xe. *Geophys Res Lett* 16:81-84
- Mazor E, Heymann D, Anders E (1970) Noble gases in carbonaceous chondrites. *Geochim Cosmochim Acta* 34:781-824
- McDonough WF, Sun S-s (1995) The composition of the Earth. *Chem Geol* 120:223-253
- McElroy MB, Prather MJ (1981) Noble gases in the terrestrial planets. *Nature* 293:535-539
- Melosh HJ, Vickery AM (1989) Impact erosion of the primordial atmosphere of Mars. *Nature* 338:487-489
- Mizuno H, Wetherill GW (1984) Grain abundance in the primordial atmosphere of the Earth. *Icarus* 59:74-86
- Mizuno H, Nakazawa K, Hayashi C (1980) Dissolution of the primordial rare gases into the molten Earth's material. *Earth Planet Sci Lett* 50:202-210
- Morrison P, Pine J (1955) Radiogenic origin of the helium isotopes in rock. *Ann NY Acad Sci* 62:69-92
- Musselwhite DS, Drake MJ (2000) Early outgassing of Mars: implications from experimentally determined solubility of iodine in silicate magmas. *Icarus* 148:160-175
- Musselwhite DS, Drake MJ, Swindle TD (1991) Early outgassing of Mars supported by differential water solubility of iodine and xenon. *Nature* 352:697-699
- Niedermann S, Bach W, Erzinger J (1997) Noble gas evidence for a lower mantle component in MORBs from the southern East Pacific Rise: decoupling of helium and neon isotope systematics. *Geochim Cosmochim Acta* 61:2697-2715
- Niemeyer S, Marti K (1981) Noble gas trapping by laboratory carbon condensates. *Proc 12th Lunar Planet Sci Conf*, p 1177-1188
- Notesco G, Laufer D, Bar-Nun A, Owen T (1999) An experimental study of isotopic enrichments in Ar, Kr, and Xe when trapped in water ice. *Icarus* 142, 298-300

- Ott U (1988) Noble gases in SNC meteorites: Shergotty, Nakhla, Chassigny. *Geochim Cosmochim Acta* 52:1937-1948
- Ott U (2002) Noble gases in meteorites- trapped components. *Rev Mineral Geochem* 47:71-100
- Owen T (1987) Could icy impacts reconcile Venus with Earth and Mars? *In Mars: Evolution of its Climate and Atmosphere*. Baker V, Carr M, Fanale F, Greeley R, Haberle R, Leovy C, Maxwell T (eds) LPI Tech Report 87-01, Lunar Planet Inst, Houston, Texas, p 91
- Owen T, Bar-Nun A (1995a) Comets, impacts and atmospheres. *Icarus* 116:215-226
- Owen T, Bar-Nun A (1995b) Comets, impacts and atmospheres II. Isotopes and noble gases. *In Volatiles in the Earth and Solar System*. Farley KA (ed), Am Inst Phys Conf Proc 341:123-138
- Owen T, Bar-Nun A, Kleinfeld I (1991) Noble gases in terrestrial planets: Evidence for cometary impacts? *In Comets in the Post-Halley Era*. Vol. 1. Newburn Jr RL, Neugebauer M, Rahe J (eds) Kluwer Academic Publications, Dordrecht, The Netherlands, p 429-437
- Owen T, Bar-Nun A, Kleinfeld I (1992) Possible cometary origin of heavy noble gases in the atmospheres of Venus, Earth and Mars. *Nature* 358:43-46
- Ozima M, Igarashi G (1989) Terrestrial noble gases: Constraints and implications on atmospheric evolution. *In Origin and Evolution of Planetary and Satellite Atmospheres*. Atreya SK, Pollack JB, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 306-327
- Ozima M, Igarashi G (2000) The primordial noble gases in the Earth: a key constraint on Earth evolution models. *Earth Planet Sci Lett* 176:219-232
- Ozima M, Nakazawa K (1980) Origin of rare gases in the Earth. *Nature* 284:313-316
- Ozima M, Podosek FA (1999) Formation age of Earth from $^{129}\text{I}/^{127}\text{I}$ and $^{244}\text{Pu}/^{238}\text{U}$ systematics and the missing Xe. *J Geophys Res* 104:25493-25499
- Ozima M, Podosek FA (2001) *Noble Gas Geochemistry* 2nd edn. Cambridge, Cambridge University Press, Cambridge
- Ozima M, Zahnle K (1993) Mantle degassing and atmospheric evolution: Noble gas view. *Geochem J* 27:185-200
- Ozima M, Wieler R, Marty B, Podosek FA (1998) Comparative studies of solar, Q-gases and terrestrial noble gases, and implications on the evolution of the solar nebula. *Geochim Cosmochim Acta* 62:301-314
- Palma RL, Becker RH, Pepin RO, Schlutter DJ (2002) Irradiation records in regolith materials, II: Solar-wind and solar-energetic-particle components in helium, neon, and argon extracted from single lunar mineral grains and from the Kapoeta howardite by stepwise pulse-heating. *Geochim Cosmochim Acta* (in press)
- Pavlov AA, Pavlov AK, Kasting JF (1999) Irradiated interplanetary dust particles as a possible solution for the deuterium/hydrogen paradox of Earth's oceans. *J Geophys Res* 104:30725-30728
- Pepin RO (1989) On the relationship between early solar activity and the evolution of terrestrial planet atmospheres. *In The Formation and Evolution of Planetary Systems*. Weaver HA, Danly L (eds) Space Tel Sci Inst Symp Series #3, Cambridge University Press, New York p 55-74
- Pepin RO (1991) On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. *Icarus* 92:2-79
- Pepin RO (1992) Origin of noble gases in the terrestrial planets. *Ann Rev Earth Planet Sci* 20: 389-430
- Pepin RO (1994) Evolution of the martian atmosphere. *Icarus* 111:289-304
- Pepin RO (1997) Evolution of Earth's noble gases: Consequences of assuming hydrodynamic loss driven by giant impact. *Icarus* 126:148-156
- Pepin RO (1998) Isotopic evidence for a solar argon component in the Earth's mantle. *Nature* 394:664-667
- Pepin RO (2000) On the isotopic composition of primordial xenon in terrestrial planet atmospheres. *Space Sci Rev* 92:371-395
- Pepin RO (2002) Generation of meteoritic noble gas isotope ratios by hydrodynamic escape of transient degassed atmospheres on planetesimals. *Meteorit Planet Sci* in press (abstract)
- Pepin RO, Carr MH (1991) Major issues and outstanding questions. *In Mars*. Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 120-143
- Pepin RO, Phinney D (1976) The formation interval of the Earth. *Lunar Sci VII*:682-684
- Pepin RO, Becker RH, Rider PE (1995) Xenon and krypton isotopes in extraterrestrial regolith soils and in the solar wind. *Geochim Cosmochim Acta* 59:4997-5022
- Pepin RO, Becker RH, Schlutter DJ (1999) Irradiation records in regolith materials, I: Isotopic compositions of solar-wind neon and argon in single lunar mineral grains. *Geochim Cosmochim Acta* 63:2145-2162
- Phinney D (1972) ^{36}Ar , Kr, and Xe in terrestrial materials. *Earth Planet Sci Lett* 16:413-420
- Phinney D, Tennyson J, Frick U (1978) Xenon in CO_2 well gas revisited. *J Geophys Res* 83:2313-2319
- Podosek FA, Cassen P (1994) Theoretical, observational, and isotopic estimates of the lifetime of the solar nebula. *Meteoritics* 29:6-25

- Podosek FA, Honda M, Ozima M (1980) Sedimentary noble gases. *Geochim Cosmochim Acta* 44:1875-1884
- Podosek FA, Bernatowicz TJ, Kramer FE (1981) Adsorption of xenon and krypton on shales. *Geochim Cosmochim Acta* 45:2401-2415
- Podosek FA, Woolum DS, Cassen P, Nichols RH (2000) Solar gases in the Earth by solar wind irradiation? *J Conf Abstr* 5:804
- Porcelli D, Ballentine CJ (2002) Models for the distribution of terrestrial noble gases and the evolution of the atmosphere. *Rev Mineral Geochem* 47:411-480
- Porcelli D, Halliday AN (2001) The core as a possible source of mantle helium. *Earth Planet Sci Lett* 192:45-56
- Porcelli D, Pepin RO (2000) Rare gas constraints on early Earth history. *In* *Origin of the Earth and Moon*. Canup RM, Righter K (eds) University of Arizona Press, Tucson, Arizona, p 435-458
- Porcelli D, Wasserburg GJ (1995a) Mass transfer of xenon through a steady-state upper mantle. *Geochim Cosmochim Acta* 59:1991-2007
- Porcelli D, Wasserburg GJ (1995b) Mass transfer of helium, neon, argon, and xenon through a steady-state upper mantle. *Geochim Cosmochim Acta* 59:4921-4937
- Porcelli D, Wasserburg GJ (1995c) A unified model for terrestrial rare gases. *In* *Volatiles in the Earth and Solar System*. Farley KA (ed), *Am Inst Phys Conf Proc* 341:56-69
- Porcelli DR, Woolum D, Cassen P (2001) Deep Earth rare gases: initial inventories, capture from the solar nebula, and losses during Moon formation. *Earth Planet Sci Lett* 193:237-251
- Prinn RG, Fegley B Jr (1989) Solar nebula chemistry: Origin of planetary, satellite, and cometary volatiles. *In* *Origin and Evolution of Planetary and Satellite Atmospheres*. Atreya SK, Pollack JB, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 78-136
- Safronov VS (1978) The heating of the Earth during its formation. *Icarus* 33:1-12
- Sarda P, Staudacher T, Allègre CJ (1985) $^{40}\text{Ar}/^{36}\text{Ar}$ in MORB glasses: constraints on atmosphere and mantle evolution. *Earth Planet Sci Lett* 72:357-375
- Sarda P, Staudacher T, Allègre CJ (1988) Neon isotopes in submarine basalts. *Earth Planet Sci Lett* 91:73-88
- Sasaki S (1991) Off-disk penetration of ancient solar wind. *Icarus* 91:29-38
- Sasaki S (1999) Presence of a primary solar-type atmosphere around the Earth: evidence of dissolved noble gas. *Planet Space Sci* 47:1423-1431
- Sasaki S, Nakazawa K (1988) Origin of isotopic fractionation of terrestrial Xe: hydrodynamic fractionation during escape of the primordial H_2 -He atmosphere. *Earth Planet Sci Lett* 89:323-334
- Sasaki S, Nakazawa K (1990) Did a primary solar-type atmosphere exist around the proto-Earth? *Icarus* 85:21-42
- Sasaki S, Tajika E (1995) Degassing history and evolution of volcanic activities of terrestrial planets based on radiogenic noble gas degassing models. *In* *Volatiles in the Earth and Solar System*. Farley KA (ed) *Am Inst Phys Conf Proc* 341:186-199
- Shibata T, Takahashi E, Matsuda J (1998) Solubility of neon, argon, krypton, and xenon in binary and ternary silicate systems: A new view on noble gas solubility. *Geochim Cosmochim Acta* 62:1241-1253
- Signer P, Suess HE (1963) Rare gases in the sun, in the atmosphere, and in meteorites. *In* *Earth Science and Meteoritics*. Geiss J, Goldberg ED (eds) North-Holland, Amsterdam p 241-272
- Simon T, Herbig G, Boesgaard AM (1985) The evolution of chromospheric activity and the spin-down of solar-type stars. *Astrophys J* 293:551-574
- Strom SE, Strom KM, Edwards S (1988) Energetic winds and circumstellar disks associated with low mass young stellar objects. *In* *NATO Advanced Study Institute: Galactic and Extragalactic Star Formation*. Pudritz R (ed) D. Reidel, Dordrecht, The Netherlands p 53-68
- Strom SE, Edwards S, Skrutskie MF (1993) Evolutionary timescales for circumstellar disks associated with intermediate- and solar-type stars. *In* *Protostars and Planets III*. Levy EH, Lunine JI (eds) University of Arizona Press, Tucson, Arizona, p 837-866
- Suess HE (1949) The abundances of noble gases in the Earth and Cosmos. *J Geol* 57:600-607 (in German)
- Swindle TD (2002) Martian noble gases. *Rev Mineral Geochem* 47:171-190
- Swindle TD, Jones JH (1997) The xenon isotopic composition of the primordial Martian atmosphere: Contributions from solar and fission components. *J Geophys Res* 102:1671-1678
- Swindle TD, Caffee MW, Hohenberg CM (1986) Xenon and other noble gases in shergottites. *Geochim Cosmochim Acta* 50:1001-1015
- Tajika E, Sasaki S (1996) Magma generation on Mars constrained from an Ar-40 degassing model. *J Geophys Res* 101:7543-7554
- Tolstikhin IN, O'Nions RK (1994) The Earth's missing xenon: A combination of early degassing and of rare gas loss from the atmosphere. *Chem Geol* 115:1-6

- Tonks WB, Melosh HJ (1990) The physics of crystal settling and suspension in a turbulent magma ocean. *In* Origin of the Earth. Newsom HE, Jones JH (eds) Oxford University Press, Oxford, p 151-171
- Torgersen T (1989) Terrestrial helium degassing fluxes and the atmospheric helium budget: implications with respect to the degassing processes of continental crust. *Chem Geol* 79:1-14
- Trieloff M, Kunz J, Clague DA, Harrison D, Allègre CJ (2000) The nature of pristine noble gases in mantle plumes. *Science* 288:1036-1038
- Trieloff M, Kunz J, Clague DA, Harrison D, Allègre CJ (2001) Reply to comment on noble gases in mantle plumes. *Science* 291:2269a
- Trieloff M, Kunz J, Allègre CJ (2002) Noble gas systematics of the Réunion mantle plume source and the origin of primordial noble gases in Earth's mantle. *Earth Planet Sci Lett* 200:297-313
- Turcotte DL, Schubert G (1988) Tectonic implications of radiogenic noble gases in planetary atmospheres. *Icarus* 74:36-46
- Tyburczy JA, Frisch B, Ahrens TJ (1986) Shock-induced volatile loss from a carbonaceous chondrite: implications for planetary accretion. *Earth Planet Sci Lett* 80:201-207
- Valbracht PJ, Staudacher T, Malahoff A, Allègre CJ (1997) Noble gas systematics of deep rift zone glasses from Loihi Seamount, Hawaii. *Earth Planet Sci Lett* 150: 399-411
- van Keken PE, Hauri EH, Ballentine CJ (2002) Mixing in the mantle and the creation, preservation and destruction of mantle heterogeneity. *Ann Rev Earth Planet Sci* 30:493-525
- Vickery AM, Melosh HJ (1990) Atmospheric erosion and impactor retention in large impacts with application to mass extinctions. *In* Global Catastrophes in Earth History. Sharpton VL, Ward PD (eds) *Geol Soc Am Spec Paper* 247:289-300
- Volkov VP, Frenkel MY (1993) The modelling of Venus degassing in terms of K-Ar system. *Earth Moon Planets* 62:117-129
- von Zahn U, Kumar S, Niemann H, Prinn R (1983) Composition of the Venus atmosphere. *In* Venus. Hunten D, Colin L, Donahue T, Moroz V (eds) University of Arizona Press, Tucson, Arizona, p 299-430
- Wacker JF (1989) Laboratory simulation of meteoritic noble gases. III. Sorption of neon, argon, krypton and xenon on carbon: Elemental fractionation. *Geochim Cosmochim Acta* 53:1421-1433
- Wacker JF, Anders E (1984) Trapping of xenon in ice: implications for the origin of the Earth's noble gases. *Geochim Cosmochim Acta* 48:2373-2380
- Wacker JF, Zadnik MG, Anders E (1985) Laboratory simulation of meteoritic noble gases. I. Sorption of xenon on carbon: Trapping experiments. *Geochim Cosmochim Acta* 49:1035-1048
- Walter FM, Barry DC (1991) Pre- and main sequence evolution of solar activity. *In* The Sun in Time. Sonett CP, Giampapa MS, Matthews MS (eds) University of Arizona Press, Tucson, Arizona, p 633-657
- Walter FM, Brown A, Mathieu RD, Myers PC, Vrba FJ (1988) X-ray sources in regions of star formation. III. Naked T Tauri stars associated with the Taurus-Auriga complex. *Astron J* 96:297-325
- Wänke H, Dreibus G (1988) Chemical composition and accretion history of terrestrial planets. *Phil Trans R Soc London A325:545-557*
- Wasson JT, Kallemeyn GW (1988) Composition of chondrites. *Phil Trans Roy Soc Lond A325:535-544*
- Wetherill GW (1954) Variations in the isotopic abundances of neon and argon extracted from radioactive minerals. *Phys Rev* 96:679-683
- Wetherill GW (1975) Radiometric chronology of the early solar system. *Ann Rev Nucl Sci* 25:283-328
- Wetherill GW (1981) Solar wind origin of ^{36}Ar on Venus. *Icarus* 46:70-80
- Wetherill GW (1986) Accumulation of the terrestrial planets and implications concerning lunar origin. *In* Origin of the Moon. Hartmann WK, Phillips RJ, Taylor GJ (eds) Lunar and Planetary Institute, Houston, p 519-550
- Wetherill GW (1990a) Formation of the Earth. *Ann Rev Earth Planet Sci* 18:205-256
- Wetherill GW (1990b) Calculation of mass and velocity distributions of terrestrial and lunar impactors by use of theory of planetary accumulation. *In* Abstracts for the International Workshop on Meteorite Impact on the Early Earth, LPI Contrib 746. Lunar and Planetary Institute, Houston, Texas, p 54-55
- Wetherill GW, Stewart GR (1993) Formation of planetary embryos: Effects of fragmentation, low relative velocity, and independent variation of eccentricity and inclination. *Icarus* 106:190-209
- Wieler R (1994) "Q-gases" as "local" primordial noble gas component in primitive meteorites. *In* Noble gas geochemistry and cosmochemistry. Matsuda J (ed) Terra Scientific Publishing, Tokyo, p 31-41
- Wieler R (2002) Noble gases in the solar system. *Rev Mineral Geochem* 47:21-70:
- Wieler R, Baur H (1994) Krypton and xenon from the solar wind and solar energetic particles in two lunar ilmenites of different antiquity. *Meteoritics* 29:570-580
- Woolum DS, Cassen P, Porcelli D, Wasserburg GJ (1999) Incorporation of solar noble gases from a nebula-derived atmosphere during magma ocean cooling. *Lunar and Planetary Science XXX*, Lunar and Planetary Institute, Houston abstract #1518 (CD-ROM)

- Yang J, Anders E (1982a) Sorption of noble gases by solids, with reference to meteorites. II. Chromite and carbon. *Geochim Cosmochim Acta* 46:861-875
- Yang J, Anders E (1982b) Sorption of noble gases by solids, with reference to meteorites. III. Sulfides, spinels, and other substances; on the origin of planetary gases. *Geochim Cosmochim Acta* 46:877-892
- Yang J, Lewis RS, Anders E (1982) Sorption of noble gases by solids, with reference to meteorites. I. Magnetite and carbon. *Geochim Cosmochim Acta* 46:841-860
- Zadnik MG, Wacker JF, Lewis RS (1985) Laboratory simulation of meteoritic noble gases. II. Sorption of xenon on carbon: Etching and heating experiments. *Geochim Cosmochim Acta* 49:1049-1059
- Zahnle KJ (1993) Xenological constraints on the impact erosion of the early martian atmosphere. *J Geophys Res* 98:10899-10913
- Zahnle KJ, Kasting JF (1986) Mass fractionation during transonic escape and implications for loss of water from Mars and Venus. *Icarus* 68:462-480
- Zahnle KJ, Kasting JF, Pollack JB (1990a) Mass fractionation of noble gases in diffusion-limited hydrodynamic hydrogen escape. *Icarus* 84:502-527
- Zahnle KJ, Pollack JB, Kasting JF (1990b) Xenon fractionation in porous planetesimals. *Geochim Cosmochim Acta* 54:2577-2586
- Zhang MHG, Luhmann JG, Bougher SW, Nagy AF (1993) The ancient oxygen exosphere of Mars: Implications for atmospheric evolution. *J Geophys Res* 98:10915-10923
- Zhang Y, Zindler A (1989) Noble gas constraints on the evolution of the Earth's atmosphere. *J Geophys Res* 94:13719-13737