

CONTRIBUTIONS OF ICY PLANETESIMALS TO THE EARTH'S EARLY ATMOSPHERE

Invited paper

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Abstract. Laboratory experiments on the trapping of gases by ice forming at low temperatures implicate comets as major carriers of the heavy noble gases to the inner planets. These icy planetesimals may also have brought the nitrogen compounds that ultimately produced atmospheric N₂. However, if the sample of three comets analyzed so far is typical, the Earth's oceans cannot have been produced by comets alone, they require an additional source of water with low D/H. The highly fractionated neon in the Earth's atmosphere may also indicate the importance of non-icy carriers of volatiles. The most important additional carrier is probably the rocky material comprising the bulk of the mass of these planets. Venus may require a contribution from icy planetesimals formed at the low temperatures characteristic of the Kuiper Belt.

1. Introduction

As soon as he had successfully calculated cometary orbits, Edmund Halley (1687) realized that collisions of comets with the Earth were a real possibility and might have remarkable consequences. In more modern times, Oro (1961) proposed that comets could have been an important source of pre-biotic organic material, and other investigators have suggested that these icy planetesimals might have made major contributions to our planet's atmosphere (e.g., Sill and Wilkening, 1978; Delsemme, 1991, 2000). Recent work on this question has focused on models of the dissipation of icy planetesimals from the Uranus-Neptune region as these planets finished forming (Levison *et al.*, 1999), or attempts to calculate the extent of the terrestrial cometary influx through analysis of the cratering record of the moon (Chyba, 1990; Delsemme, 1991, 2000). All of these studies suffer from the absence of evidence for a uniquely identifiable cometary contribution to the Earth's volatile inventory.

The difficulty in identifying the sources of the Earth's volatiles is compounded by the 4.6 billion year history of the planet, during which chemical reactions with the crust, escape of gases from the upper atmosphere and the origin and evolution of life have episodically changed the composition of the atmosphere and hydrosphere. The central problem of life's origin is intimately dependent on the nature



of the early atmosphere, making our inability to define the composition of that atmosphere all the more frustrating.

It is this dilemma that the heavy noble gases have the potential to resolve, since they are chemically inert, do not easily escape from the atmosphere, and are not involved in the activities of living organisms. The firmly entrenched idea that the atmospheric noble gas abundances (and hence other volatiles) are the result of delivery by meteorites (e.g., Turekian and Clark, 1975; Anders and Owen, 1977) stems from the recognition of a so-called 'planetary pattern' in the noble gases found in these objects many years ago. This idea gained widespread support, despite the fact that it has never been possible to explain why the abundances of krypton and xenon in the meteorites are about the same, while xenon is ~ 20 times less abundant than krypton in the Earth's atmosphere (Figure 1). Attempts to find the 'missing' xenon buried in the sedimentary column, clathrates or ice have failed (Wacker and Anders, 1984; Bernatowicz *et al.*, 1985). Furthermore, the relative abundances of the isotopes in atmospheric xenon are distinctly different from those in meteorites (or the solar wind) (Figure 2). These difficulties with meteoritic xenon coupled with the arguments for early cometary bombardment encouraged us to pursue the idea that icy, rather than rocky planetesimals delivered the noble gases and many other volatiles as well.

2. A Cometary Model for Delivery of Volatiles

Accordingly, we set out to determine whether or not the abundance patterns of the heavy noble gases in the atmospheres of the inner planets could be accounted for by comets. The first step was to apply the same laboratory techniques for trapping gases in amorphous ice deposited at low temperatures that had been used with N_2 , CO , H_2 , etc. (Bar-Nun *et al.*, 1985, 1988; Laufer *et al.*, 1987) to a mixture of heavy noble gases; argon, krypton and xenon (Owen *et al.*, 1991). These experiments were designed to imitate the formation of comets in the outer solar nebula. The idea was that interstellar ice grains probably sublimated as they fell toward the mid-plane of the nebula and recondensed on cold refractory cores (Lunine *et al.*, 1991; Chick and Cassen, 1997). In this re-condensation process, the ice could trap ambient gas according to the local temperature. We restricted our study to amorphous ice because we assume that the ambient temperature and pressure in the comet-forming region favor the production of ice in this state. Crystalline ice particles could form closer to the sun and might be carried outward to mix with the colder material according to Nuth *et al.* (2000). However, such ice would not capture gas unless by clathration, which has not been demonstrated to occur at these low temperatures and pressures. Furthermore, the one spectrum of ice in the nucleus of a dynamically young comet that we have indicates that the ice is in the amorphous state (Davies *et al.*, 1997).

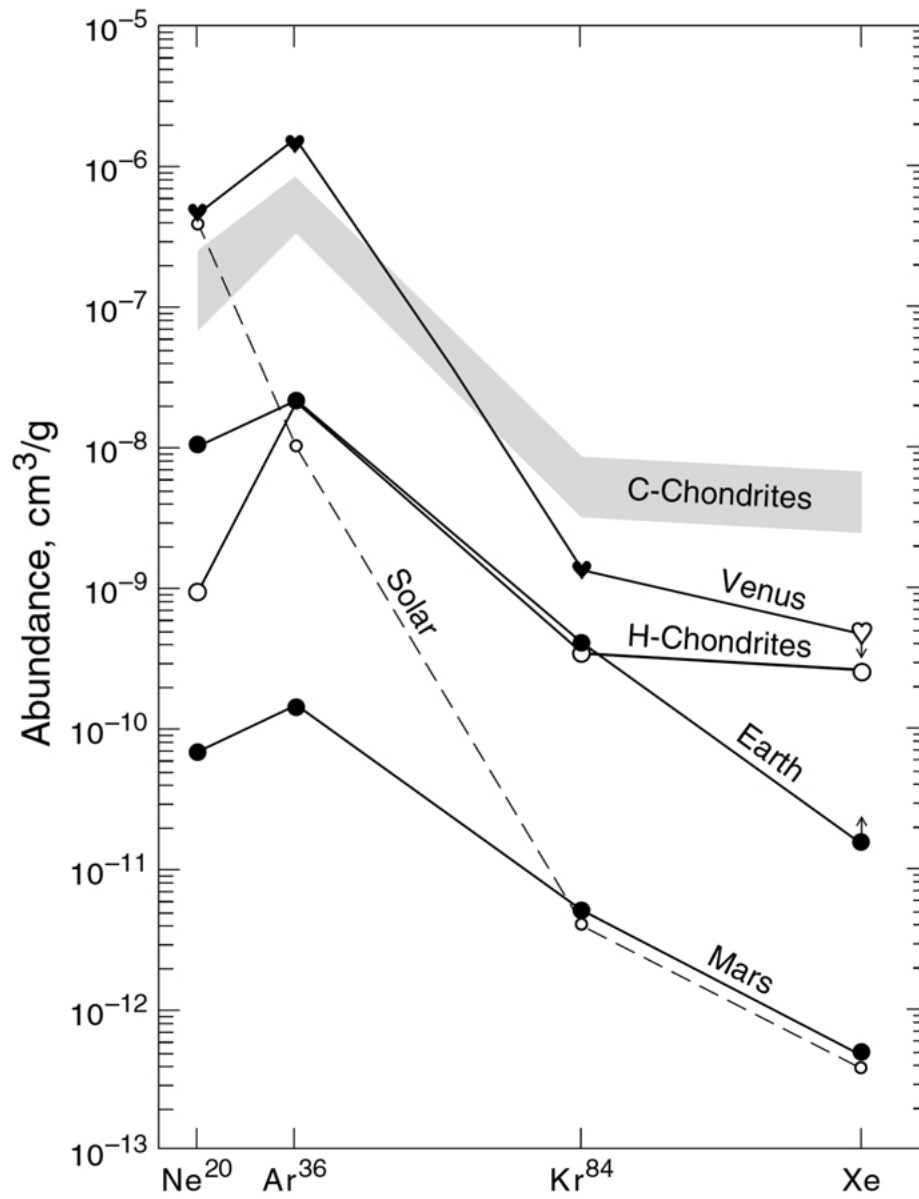


Figure 1. Chondritic meteorites contain about as much xenon as krypton. The meteoritic noble gas abundances therefore do not match the abundance patterns found in inner planet atmospheres, despite the apparent agreement for Ne, Ar, and Kr. (Solar values are normalized for ^{84}Kr on Mars). Note the high abundances of Ne and Ar per gram of rock and the solar type $^{36}\text{Ar}/^{84}\text{Kr}$ on Venus (Owen and Bar-Nun, 1995a).

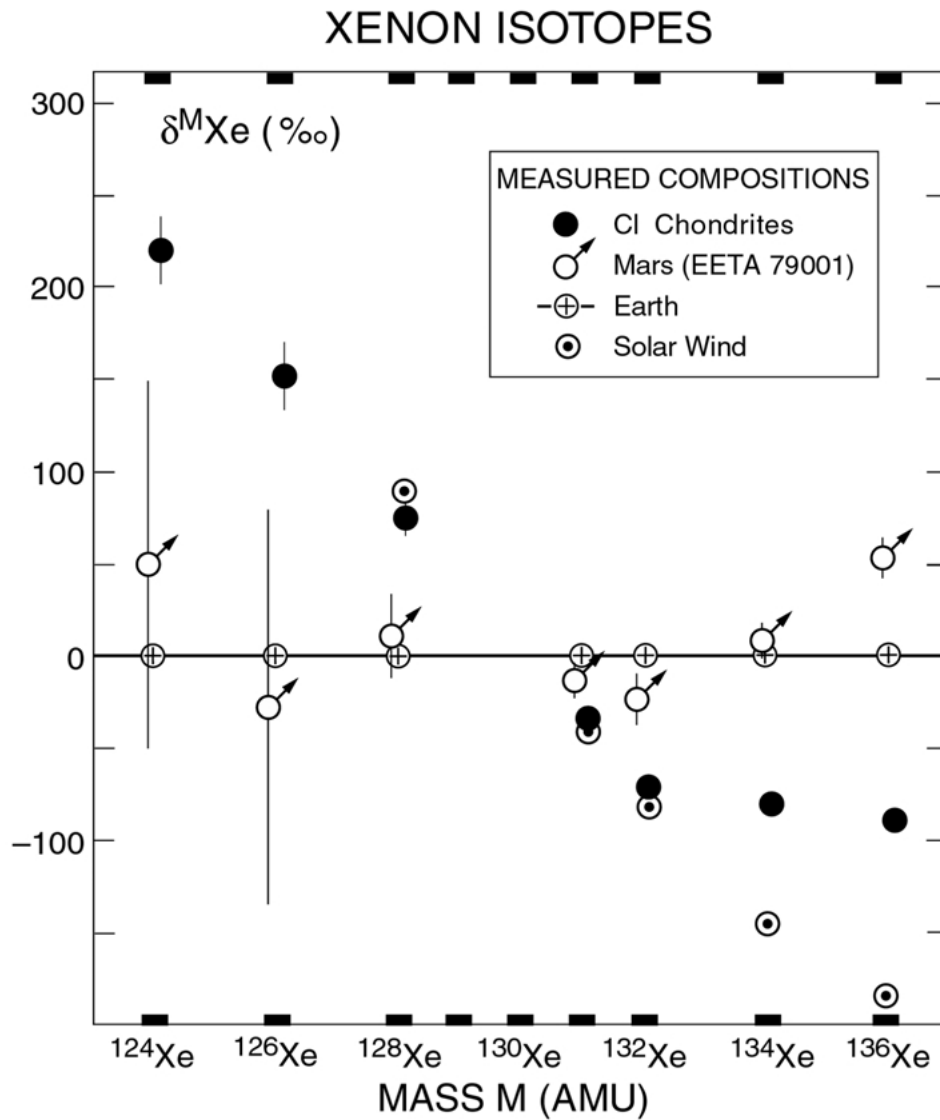


Figure 2. In this plot, the relative abundances of the xenon isotopes in the solar wind (as sampled in lunar surface materials), carbonaceous chondrites and the Martian atmosphere are compared with values in the Earth's atmosphere. We seem to have two 'families': Mars and Earth vs the sun and the chondrites. But no two sources are exactly alike (after Pepin, 1989, solar wind data from Ozima *et al.*, 1998; Mars points from Swindle *et al.*, 1986 confirmed by Garrison and Bogard, 1998).

The laboratory results showed that temperature-dependent fractionation of the gas mixtures occurs, principally the depletion of Ar, which suggested that trapping in ice might indeed be responsible for the patterns of noble gas abundances found in the atmospheres of Mars, Earth and Venus (Owen *et al.*, 1991). This initial analysis was not conclusive, however, since it did not seem possible to account for the variety of patterns observed on the three planets with a single model of cometary bombardment.

The SNC meteorites provided another clue. It is now widely accepted that these meteorites come from Mars (e.g., McSween, 1994). Yet a three-element plot of $^{36}\text{Ar}/^{132}\text{Xe}$ vs $^{84}\text{Kr}/^{132}\text{Xe}$ shows that the abundances of these gases are very different in the different meteorites, and even in different samples of the same meteorite, with abundances from S and C meteorites forming a straight line on a log-log plot (Figure 3). This line passes through points corresponding to the noble gases found in the atmospheres of the Earth and Mars, but it is widely separated from the field of abundances in chondritic meteorites or the values found in the solar wind (Ott and Begemann, 1985).

We have interpreted this distribution of noble gas abundances in the SNC meteorites as an effect of the mixing of two different reservoirs: one that represents gases trapped in the rocks that form the planets, the second a contribution from impacting icy planetesimals. This interpretation is based on our data for the fractionation of noble gases by trapping in amorphous ice (Bar-Nun *et al.*, 1988; Laufer *et al.*, 1987; Owen *et al.*, 1991). At a temperature of ~ 50 K, ice formed by condensation of water vapor traps argon, krypton and xenon in relative abundances that fall on an extrapolation of a mixing line drawn through the abundances from the atmospheres of Earth and Mars on the same three-element plot (Figure 3). The analysis is complicated by the fact that the linear relation on the log-log plot (as first illustrated by Ott and Begemann, 1985) is very close to this mixing line over the range of noble gas values determined in the Shergottites (Owen *et al.*, 1992; Ozima and Wada, 1993; Owen and Bar-Nun, 1993). It may well be that more than one process is at work here. However, we have pointed out that the increase in $^{129}\text{Xe}/^{132}\text{Xe}$ with increasing $^{36}\text{Ar}/^{132}\text{Xe}$ that occurs in the samples plotted along this same mixing line demonstrates that solubility in a melt (for example) cannot explain the data by itself (Owen and Bar-Nun, 1993).

The noble gases in the atmosphere of Venus do not conform to this simple picture. Xenon has not yet been measured on Venus, but the relative abundances of argon and krypton resemble the solar ratio (Figure 1), placing Venus somewhere in the stippled trapezoid at the top of Figure 3. As Figure 1 demonstrates, Venus exhibits higher abundances of argon and neon per gram of rock than the most volatile-rich carbonaceous chondrites. We have suggested that the heavy noble gases on Venus were contributed by one or more icy planetesimals formed at $T \leq 30$ K, i.e., objects equivalent to those populating the Kuiper Belt (Owen and Bar-Nun, 1995a). A single icy planetesimal that condensed with solar elemental abundances would need a radius of ~ 90 km to deliver the presently observed

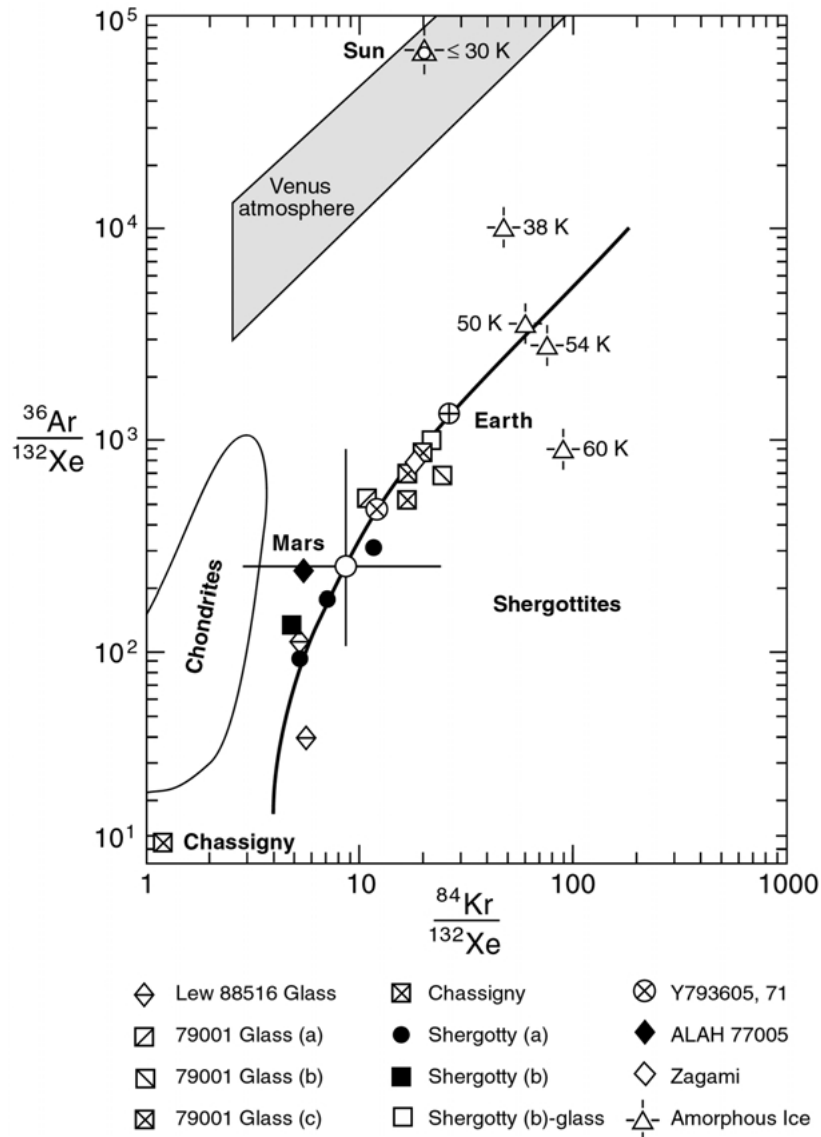


Figure 3. In a three element plot, noble gas abundances in the atmospheres of Mars (Viking) and Earth can be used to define a mixing line between internal and external volatile reservoirs. The internal reservoir lies below Mars on this plot, and consists of the rocks that formed the planet. We suggest icy planetesimals as the external reservoir, lying above the Earth mixture at the opposite end of the line. The external reservoir is represented here by the noble gases trapped in amorphous ice in laboratory experiments (the open triangles). These points correspond to solar elemental ratios multiplied by the fractionation factors found experimentally (Owen *et al.*, 1991). Noble gas abundances in Shergottites (meteorites from Mars) fall along this line. The gases on Venus could have been delivered by comets from Kuiper Belt that formed at temperatures less than 30-35 K. The abundance of Xe on Venus is not yet known, hence the stippled trapezoid. References: Shergotty (a), Chassigny: Ott, 1988; Lew 885516 glass: Beck and Pepin, 1993; ALAH 77005 79001 Glass (a): Swindle *et al.*, 1986; 79001 Glass (b): Becker and Pepin (1984); Zagami: Ott *et al.* (1988); Shergotty (b), Y 793605, 71, 79001 glass (c): Bogard and Garrison, 1998.

amount of argon. (A different approach, scaling from a now-obsolete model of Titan gave $r = 75$ km [Hunten *et al.*, 1988].) Obviously a cluster of smaller comets could achieve the same effect. Earth and Mars must have been struck by such planetesimals as well, the argument is simply that Venus was hit by a bigger one, or by more of such objects than the other two planets.

Alternatively, one could postulate that the heavy noble gases on Venus were contributed by the solar wind directly into the dust that became the rocks that formed the planet (Wetherill, 1981). The presence of this new-solar component of noble gases on Venus and not on Mars and Earth could then be explained by the lack of major, atmosphere-eroding impacts on Venus. We will discuss the neon abundance in a later section.

We have further tested the applicability of the laboratory data to natural phenomena by examining the abundances of CO and N₂ in comets. We pointed out that the apparently mysterious depletion of nitrogen in comets (Geiss, 1988; Krankowsky, 1991) probably results from the inability of ice to trap N₂ efficiently when the ice forms at $T > 35$ K. Our assumption is that most of the nitrogen that was present in the outer solar nebula was in the form of N₂, just as it is assumed to be in the interstellar medium (van Dishoeck *et al.*, 1993). Hence for comets to acquire a solar ratio of N/O, the condensing ice that formed the comets would have to trap N₂. Just as the abundance of Ar is sharply reduced in ice forming at 50 K, N₂ will be depleted as well (Bar-Nun *et al.*, 1988). Thus it is entirely consistent that comets should deliver an ensemble of volatiles that is depleted in both Ar and N, relative to solar abundances referenced to oxygen. In the Earth's volatile inventory, C/N is between 5 and 10 times the solar value.

Because of the difficulty in trapping N₂, we expect the dominant carriers of nitrogen to the inner planets (and the small, icy bodies of the outer solar system) to have been nitrogen compounds such as HCN and NH₃ and large organic molecules that are easily trapped in ice forming at temperatures of 50 K (or even higher). The isotopic composition of the nitrogen in the atmospheres of these relatively small bodies could therefore be different from that of nitrogen in the sun or in the atmospheres of the giant planets, where N₂ should have been the dominant carrier. We will return to this point below.

We also showed that the relative abundances of CO⁺/N₂⁺ derived from observations of comet tail spectra are consistent with the formation of the icy nuclei at temperatures near 50 K. Further work on the trapping of CO and N₂ in ice has substantiated our original conclusions (Notesco and Bar-Nun, 1996).

These consistencies between the laboratory results and the observed abundances in comets lent support to our effort to extrapolate laboratory work on ice trapping of noble gases to noble gas abundances in planetary atmospheres. Accordingly, we developed an 'icy impact' model for the contribution of comets to inner planet atmospheres. An immediate consequence of this model was the realization that if comets contributed the terrestrial heavy noble gases, they would not supply enough water to fill the oceans. Impact erosion might have solved this problem

by removing noble gases (plus carbon monoxide, carbon dioxide and nitrogen), (Chyba, 1990; Chyba *et al.*, 1994) but we also suggested that some water might have been contributed from another source, such as the rocks making up most of the mass of the planet (Owen and Bar-Nun, 1995a).

Turning to Mars, we showed that the present atmospheric abundance of ^{84}Kr would only correspond to the equivalent of 75 mb of CO_2 . This amount of CO_2 would give a ratio of $\text{C}/^{84}\text{Kr}$ in the atmosphere equal to the value found in the Earth's volatile reservoir and (within existing uncertainties) in the present atmosphere of Venus. While 75 mb of CO_2 is $10 \times$ the present value in the Martian atmosphere, it corresponds to a layer of water only 12 m thick over the planet's surface, an insufficient amount to account for the observed fluvial erosion (Carr, 1986; Greely, 1987). Accordingly, we invoked impact erosion as developed for Mars by Melosh and Vickery (1989), as the responsible agent for diminishing the atmosphere to the 75 mb level. We pointed out that impact erosion explains the relatively high ratios of $^{129}\text{Xe}/^{132}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ in the current Martian atmosphere (Owen *et al.*, 1977), well-illustrated in the gases trapped in the meteorites EETA 79001 and Zagami (Bogard and Johnson, 1983; Swindle *et al.*, 1986; Marti *et al.*, 1995; Garrison and Bogard, 1998). Another way to achieve this same result is by massive hydrodynamic escape of the early atmosphere, as proposed by Pepin (1991). In each case the assumption is that the radiogenic ^{129}Xe or its parent ^{129}I is protected from loss, e.g., by differential solubility (Musselwhite *et al.*, 1991), while the ^{40}K parent of ^{40}Ar is protected by its location in rocks. Production of massive amounts of carbonates and/or CO_2 adsorption in the regolith (e.g., Pollack, 1979), would remove CO_2 from the atmosphere, but it would not account for the excess ^{129}Xe and ^{40}Ar and it would leave behind large amounts of noble gases and nitrogen in the atmosphere, which are not observed.

We thus suggested a scenario in which the early atmosphere of Mars could have passed through several episodes of growth and decay, depending on the planet's bombardment history.

3. Deuterium in Comets: A Tie to the Interstellar Medium

Depending on the details of the process of sublimation and recondensation of infalling grains, in particular the time interval between these two processes, the comets that were subsequently built from these grains may have retained a good memory of interstellar chemical conditions. One way to test this assumption is to investigate the abundance of stable isotopes of common elements, as isotope ratios should not change during the comet-formation process we have described if it is sufficiently rapid. The recent appearance of two bright comets has allowed us to add to the isotopic data collected by *in situ* measurements of Comet Halley using ground-based observations at radio wavelengths.

The value of D/H is particularly sensitive to physical processes, since the mass ratio of these two stable isotopes is the largest in the periodic table. In Halley's comet, two independent investigations led to the result that $D/H = 3.2 \pm 0.1 \times 10^{-4}$ in the comet's H_2O , (Balsiger *et al.*, 1995; Eberhardt *et al.*, 1995). These studies were carried out *in situ*, with mass spectrometers on the Giotto spacecraft. Observations of Comet Hyakutake at radio and infrared wavelengths from Earth allowed the detection of lines of HDO and H_2O that led to a value of $D/H = 2.9 \pm 1.0 \times 10^{-4}$ (Bockelee-Morvan *et al.*, 1998). Similar investigations of Comet Hale-Bopp found $(D/H) = 3.3 \pm 0.8 \times 10^{-4}$ in H_2O (Meier *et al.*, 1998a). We thus have three Oort cloud comets exhibiting a value of D/H in H_2O that is essentially twice the value of 1.56×10^{-4} in Standard Mean Ocean Water (SMOW).

In the case of Comet Hale-Bopp, it was possible to use these same remote sensing techniques to determine D/H in HCN (Meier *et al.*, 1998b). The results were quite different: $(D/H)_{HCN} = 23 \pm 4 \times 10^{-4}$. This is exactly the kind of difference between D/H in different molecular species that shows up in interstellar molecular clouds (Millar *et al.*, 1989), providing a strong case for the preservation of interstellar chemistry in comet ices. If comets had formed from solar nebula gas that was warmed and homogenized by radial mixing, the value of D/H in both molecules would be much lower and identical, as the HCN and H_2O would exchange D with the huge reservoir of H_2 in the solar nebula, in which $D/H = 0.26 \pm 0.07 \times 10^{-4}$ (Mahaffy *et al.*, 1998) (Figure 4).

A simple ion-molecule reaction scheme appropriate for interstellar clouds suggests a formation temperature of 30 ± 10 K for H_2O and HCN in order to produce the observed values of D/H (Meier *et al.*, 1998b; Millar *et al.*, 1989). This is noticeably higher than the canonical value of 10 K for the interiors of dark clouds, but it would be appropriate for a warm clump near a 'hot core' in a cloud in which star formation is going on. This temperature is also consistent with values derived from measurements of the ortho-para ratio of hydrogen in comets (Mumma *et al.*, 1993; Crovisier *et al.*, 1997). Both the isotope ratios and the ortho-para ratio could remain constant during the simple sublimation and recondensation that takes place as icy grains settle into the disk of the solar nebula. However, the temperature at which recondensation occurs will determine how gases are trapped in the ices (Bar-Nun *et al.*, 1985; Owen and Bar-Nun, 1995a; Notesco and Bar-Nun, 1996). Hence it is not unreasonable to find solar nebula temperatures deduced from noble gas abundances to be 20 to 30 degrees higher than the original interstellar cloud (grain formation) temperatures deduced from the isotope and ortho-para ratios.

4. The Origin of Water on Earth and Mars

We might also expect to see signs of cometary bombardment in the water that is present on the inner planets. Note that all three of the comets that have been studied exhibit a value of D/H in ice that is twice the value found in ocean water on Earth.

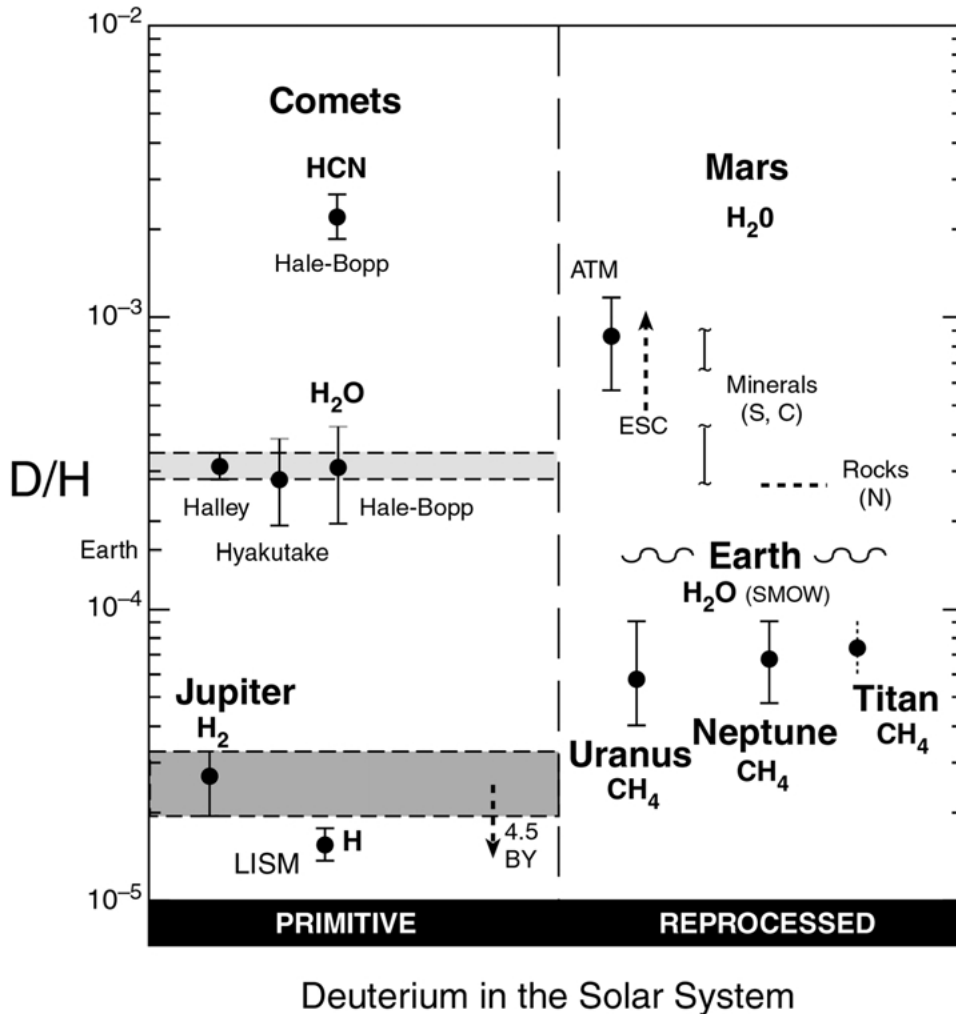


Figure 4. We can divide deuterium in the solar system into primitive (left) and reprocessed (right) reservoirs. D/H in the hydrogen gas that dominated the solar nebula can now be measured in the atmosphere of Jupiter (Mahaffy *et al.*, 1998). As expected, it is higher than the contemporary value in the Local Interstellar Medium (LISM) (Linsky, 1996), which reflects the decrease in D/H over 4.6 BY resulting from stellar nucleosynthesis in the galaxy. The much higher values of D/H in primitive condensed matter are revealed in studies of comets (see Meier and Owen, 1999 for review and data sources). Exchange between hydrogen gas and volatalized condensed matter can produce a variety of D/H values, as illustrated in the right panel of the figure. The points above terrestrial SMOW are from Martian rocks (Nakhlites) and minerals in Shergottites and Chassigny, referenced in the text. The Uranus and Neptune and Titan points come from recent observations with the Infrared Space Observatory (Feuchtgruber *et al.*, 1999; Coustenis, 1999).

All of these comets come from the Oort Cloud, a spherical shell of cometary nuclei whose average radius is 50,000 times the Earth's distance from the sun. There is certainly a tiny number compared to the 10^{11} comets that may be present in the Oort Cloud, so one might speculate that other comets may have different values of D/H. Moreover, we have not yet sampled any comets from the Kuiper Belt, a disk of comet nuclei extending outward from Neptune. The Kuiper Belt is currently thought to be the likely source of short period comets, which are unfortunately too faint to yield values of D/H to present ground-based techniques. However, these are the easiest comets for us to explore with spacecraft, because their orbits are so well known. As a result, several missions will visit short period comets in the next decade.

Meanwhile, we shall assume that the three comets that have been examined are indeed representative and see whether we can find traces of cometary water on the inner planets. Mars is the best case, because the atmosphere is so thin. The total amount of water that exchanges seasonally through the Martian atmosphere from pole to pole is just 2.9×10^{15} gm, equivalent to a single comet nucleus (density $\rho = 0.5 \text{ g cm}^{-3}$) with a radius of only 1 km. Hence the impact of a relatively small comet could have a significant effect on the surface water supply. Indications of such an effect can be found in studies of D/H in hydrous phases of the SNC meteorites. Watson *et al.* (1994) reported a range of values of D/H in kaersutite, biotite and apatite in Chassigny, Shergotty and Zagami, with the highest values, 4 to 5.5 times SMOW, occurring in Zagami apatite. Infrared spectroscopy from Earth has determined D/H in Martian atmospheric water vapor to be $5.5 \pm 2 \times$ terrestrial (Owen *et al.*, 1988; Krasnopolsky *et al.*, 1997a). Note that Zagami is one of the Shergottites with glassy inclusions containing the high values of $^{129}\text{Xe}/^{132}\text{Xe}$ clearly associated with trapped Martian atmosphere (Marti *et al.*, 1995). The overlap between the Zagami apatite and Mars atmosphere values of D/H indicates that some mixing between atmospheric water vapor and the crustal rocks must occur. It is therefore arresting to note that the *lowest* values of D/H measured in the SNC minerals do not cluster around $1 \times$ terrestrial, but rather around $\sim 2 \times$ terrestrial, the value measured in the three comets (Figure 4). It thus appears possible that most of the near-surface water on Mars accumulated after the end of the early bombardment phase and was contributed primarily by cometary impact rather than by magma from the planet or by meteoritic contributions.

This interpretation is consistent with the geochemical analysis by Carr and Wänke (1992) who concluded that Mars is much drier than the Earth, with roughly 35 ppm water in mantle rocks as opposed to 150 ppm for Earth. These authors suggested that one possible explanation for this difference is the lack of plate tectonics on Mars which would prevent a volatile-rich veneer from mixing with mantle rocks. This is exactly what the D/H values in the SNC minerals appear to signify.

In whole rock samples, D/H in water from the Shergottites is systematically higher than in Nakhla and Chassigny (Leshin *et al.*, 1996). This could be a result

of the larger fraction of atmospheric H₂O incorporated in the Shergottites by shock, a process Nakhilites evidently avoided (Bogard *et al.*, 1986; Ott, 1988; Drake *et al.*, 1994). Furthermore, higher values of $\Delta^{17}\text{O}$ are found in these samples of Nakhla and Chassigny compared with the Shergottites, reinforcing the idea that the Shergottites sampled a different source of water. Finally, the oxygen isotope ratios in water from whole rock samples of the SNCs are also systematically different from the ratios found in silicates in these rocks (Karlsson *et al.*, 1992) again suggesting a hydrosphere that is not strongly coupled to the lithosphere.

On Earth, oxygen isotopes in sea water match those in the silicates, indicating thorough mixing for at least the last 3.5 BY (Robert *et al.*, 1992). The Earth has also lost relatively little hydrogen to space after the postulated early hydrodynamic escape (Zahnle *et al.*, 1990; Pepin, 1991, 1997) so the value of D/H we measure in sea water today must be close to the original value. Yung and Dissly (1992) estimate an increase of $(\text{D}/\text{H})/(\text{D}/\text{H})_0 = 1.006$. If Halley, Hyakutake and Hale-Bopp are truly representative of all comets, then we can't make the oceans out of melted comets alone. This is a very different situation from Mars. It suggests that water from the inner reservoir, the rocks making up the bulk of the Earth, must have mixed with incoming cometary water to produce our planet's oceans. On Mars, this mixing was apparently much less efficient.

Explanations for the relatively high value of O/C (12 ± 6) in the terrestrial volatile inventory also suggest such mixing (Owen and Bar-Nun, 1995a). The solar value of O/C = 2.4, which was also the value found in Halley's comet (Geiss, 1988). Impact erosion on the Earth could remove CO and CO₂ while having less effect on water in the oceans or polar caps, thereby raising the value of O/C (Chyba, 1990; Owen and Bar-Nun, 1995a). This process would not affect the value of D/H, however. The average value of D/H in chondritic meteorites is close to that in sea water, so mixing meteoritic and cometary water would not lead to the right result. We need a contribution from a reservoir of water that is grossly deficient in C and N, with $\text{D}/\text{H} < 1.6 \times 10^{-4}$. Lecluse and Robert (1994) have shown that water vapor in the solar nebula at 1 AU from the sun would have developed a value of $\text{D}/\text{H} \approx 0.8 \times 10^{-4}$ to 1.0×10^{-4} , depending on the lifetime of the nebula (2×10^5 to 2×10^6 yr). An ocean made of roughly 35% cometary water and 65% water from the local solar nebula (trapped in planetary rocks) would satisfy the D/H constraint and would also be consistent with the observed value of O/C = 12 ± 6 .

To accept this idea, we should be able to demonstrate that water vapor from the solar nebula was adsorbed on grains that became the rocks that formed the planets. Robert (1977) has reported $\text{D}/\text{H} = 0.8 \times 10^{-4}$ in water from some meteorites. This is an indication that low D/H water was present in the inner solar system. However, our best hope for finding some of that original inner-nebula water appears to be on Mars, where mixing between the surface and the mantle has been so poor. The test is thus to look for water incorporated in SNC meteorites that appear to have trapped only mantle gases, to see if $\text{D}/\text{H} < 1.6 \times 10^{-4}$. The best case for such a test among the rocks we have is Chassigny, which exhibits no enrichment of ¹²⁹Xe

and thus appears not to have trapped any atmospheric gas. However, there is no evidence of water with low D/H in this rock (Leshin *et al.*, 1996). It may be that contamination by terrestrial water has masked the Martian mantle component in Chassigny. This is a good project for a sample returned from Mars by spacecraft, where such contamination can be avoided.

Pavlov *et al.* (1999) have proposed an alternative means of lowering the D/H ratio in cometary water delivered to Earth, viz., the early impact of H-carrying interplanetary dust particles (IDPs). This hypothesis is also testable by investigation of Martian samples if it is possible to obtain rocks excavated from different depths below the crust by large impacts.

5. The Importance of Neon and Nitrogen

We have concentrated our analysis on water and the heavy noble gases: argon, krypton and xenon. Any model for the origin of the atmosphere must also account for neon and nitrogen. Neon has about the same cosmic abundance as nitrogen relative to hydrogen (Anders and Grevesse, 1989), viz., 1.2×10^{-4} vs 1.1×10^{-4} . Hence we expect any atmosphere that consists of a captured remnant of the solar nebula to exhibit a ratio of $\text{Ne}/\text{N}_2 \approx 2$. On Earth, Mars and Venus, $\text{Ne} \ll \text{N}_2$. The neon is not only deficient in these atmospheres, the isotopes have been highly fractionated. The solar ratio of $^{20}\text{Ne}/^{22}\text{Ne} = 13.8 \pm 0.1$ (Benkert *et al.*, 1993), while on Earth $^{20}\text{Ne}/^{22}\text{Ne} = 9.8$, on Venus 11.8 ± 0.7 (Istomin *et al.*, 1982) and on Mars 10.1 ± 0.7 (Wiens *et al.*, 1986) (Figure 5-R).

The data from the nitrogen isotopes are more ambiguous. In atmospheric nitrogen on Earth, we find $^{14}\text{N}/^{15}\text{N} = 273$ (Anders and Grevesse, 1989). Direct measurements of the solar wind give $^{14}\text{N}/^{15}\text{N} = 200 \pm 55$ (Kallenbach *et al.*, 1998), whereas the most careful measurements of solar wind implanted in lunar grains give $^{14}\text{N}/^{15}\text{N} > 360$ (Hashizume *et al.*, 2000) (Figure 5, left).

As we have pointed out previously, there is a good reason to expect the solar and Earth atmosphere values to differ, viz., the atmospheric nitrogen was almost certainly delivered in the form of N-compounds, while the solar nitrogen was originally primarily (> 90%) in the form of N_2 (Owen and Bar-Nun, 1995a). This dichotomy would result from the assumed predominance of N_2 as the chief nitrogen carrier in the interstellar medium (ISM) and hence the outer solar nebula, as well as the difficulty to incorporate N_2 in icy (or rocky) planetesimals as mentioned previously.

In the local interstellar medium, $^{14}\text{N}/^{15}\text{N} = 450 \pm 100$ (Wilson and Rood, 1994; Dahmen *et al.*, 1995) (Figure 5, left). This value was determined in NH_3 and HCN : the value in N_2 , the putative main reservoir of interstellar N, remains unknown. This is because the rotational spectrum of this homonuclear molecule is forbidden and thus inaccessible to radio telescopes. However, calculations of ion-molecule reactions for N_2 and various N-compounds in the ISM indicate that the value of

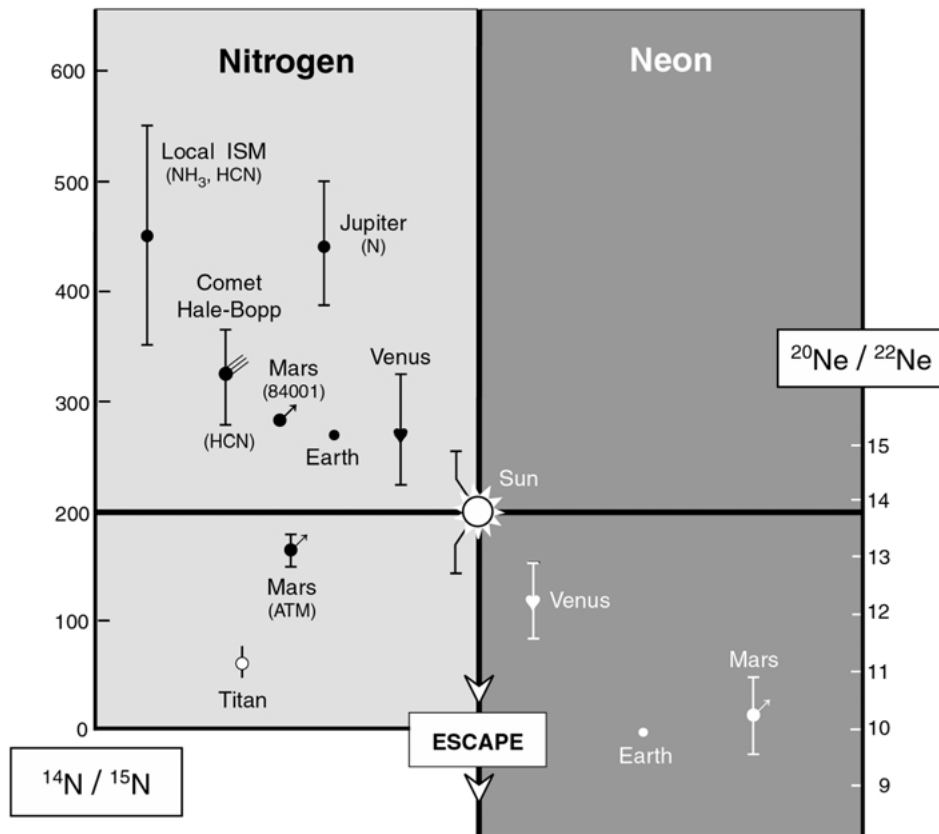


Figure 5. (Right): $^{20}\text{Ne}/^{22}\text{Ne}$ is lower on Venus, Earth and Mars compared with the solar value, presumably as a result of early atmospheric escape. (Left): In contrast, $^{14}\text{N}/^{15}\text{N}$ is higher on Earth, Venus, Comet Hale-Bopp and in NH_3 and HCN in the local interstellar medium than its value in the Sun as determined in solar wind measurements by Kallenbach *et al.* (1998). However, it now appears that the correct value of proto-solar $^{14}\text{N}/^{15}\text{N}$ is the one measured in Jupiter's atmosphere by the Galileo Probe Mass Spectrometer, while the original value in atmospheric nitrogen on the inner planets was probably closer to the value measured in Hale-Bopp's HCN (see text). The contemporary atmosphere of both Mars and Titan exhibit still lower values owing to atmospheric escape. A value similar to that in the terrestrial atmosphere has been measured in the Martian meteorite ALH 84001. (References to data points given in text).

$^{14}\text{N}/^{15}\text{N}$ in N_2 could be as high as $1.3 \times$ the value in HCN (Terzieva and Herbst, 2000). In comparing interstellar nitrogen isotope ratios with those found in the solar system, it is important to keep in mind that $^{14}\text{N}/^{15}\text{N}$ increases with time in the galaxy as ^{15}N is apparently made early, through primary production in Type II Supernova explosions, while ^{14}N is steadily produced as a secondary element in low and intermediate-mass stars. This conclusion is supported by studies of HCN in the Large Magellanic Cloud, where galactic evolution has proceeded more slowly, and $^{14}\text{N}/^{15}\text{N} = 100$ (Chin *et al.*, 1999). The best available measurement of $^{14}\text{N}/^{15}\text{N}$

in comets comes from a study of HCN by Jewitt *et al.* (1997), which gave $^{14}\text{N}/^{15}\text{N} = 323 \pm 46$. Assuming that the cometary HCN has preserved the interstellar isotopic ratio – as we have previously assumed for D/H – we would predict a value of $^{14}\text{N}/^{15}\text{N} = 1.3 \times 323 = 420$ in solar nebula N_2 . This should then be the isotope ratio we find for solar nitrogen, suggesting that the Hashizume *et al.* (2000) deduction from solar wind implanted in lunar soils is correct.

There is a further test. Jupiter should exhibit the same isotopic ratios of elements as the sun, if the uniform enhancement of heavy elements that we observe there is indeed caused by their delivery in low temperature planetesimals (Owen *et al.*, 1999). Fouchet *et al.* (2000) found $^{14}\text{N}/^{15}\text{N} = 525/ + 1500/-200$ in ISO observations of Jupiter's NH_3 , again supporting the lunar measurement but with large error bars. We have recently succeeded in extracting a value of $^{14}\text{N}/^{15}\text{N} = 435/ + 65/ - 50$ from the Galileo Probe Mass Spectrometer data (Owen *et al.*, 2001), which is probably the best value for protosolar nitrogen that we have at the present time.

Further insight can again be sought on Mars. As for H, the problem is complicated on Mars by atmospheric escape. In this case, nonthermal escape through dissociative recombination has led to an atmospheric value of $^{14}\text{N}/^{15}\text{N} = 165 \pm 15$ (Nier and McElroy, 1977) (Figure 5L). It is therefore necessary to search for light nitrogen in a 'heavy' atmospheric background. Mathew *et al.* (1998, 2000) have reported a light component in nitrogen from the Martian meteorite ALH 84001 (Figure 5L), with $^{14}\text{N}/^{15}\text{N} \geq 278$, which may be the first indication of the hypothesized cometary component.

The absence of neon-like fractionation in such a component can again be explained in terms of cometary delivery of volatiles, albeit in a paradoxical manner. The laboratory work shows that ice forming at $T = 30$ K traps less than 5×10^{-3} of the initial neon in a starting gas mixture while at $T = 50$ K, this fraction drops to $< 10^{-5}$ (Laufer *et al.*, 1987; Owen and Bar-Nun, 2001). We have therefore assumed that Oort cloud comets carry a negligible amount of Ne (Owen and Bar-Nun, 1995a). This assumption is supported by the apparent absence of neon in the atmospheres of Titan, Triton, and Pluto, where the upper limits on Ne/N_2 are typically about 0.01. Triton and Pluto represent giant icy planetesimals that can be thought of as the largest members of the Kuiper Belt. Hence the absence of detectable neon in their atmospheres may be taken as a good indication that ice condensing in the outer solar nebula did not trap significant amounts of gas, and thus we do not expect to find it in comets. (Titan is a more complicated problem because it formed in Saturn's subnebula, not in the solar nebula). This prediction is consistent with observations of Comet Hale-Bopp carried out with the Extreme Ultraviolet Explorer satellite by Krasnopolsky *et al.* (1997). These authors established an upper limit of $\text{Ne}/\text{O} < 1/200 \times \text{solar}$ in the comet.

If the comets don't carry neon, how did this gas reach the inner planets? Once again the meteorites don't help. Even if they brought in all the xenon, the neon they could deliver would be $< 10\%$ of what we observe. Instead it seems likely that on Mars and Earth, neon was brought in by the rocks, the internal reservoir we have

discussed above. In fact, we have evidence that this was the case, because we can still find neon whose isotope abundances approach the solar ratio in rocks derived from the mantle (Craig and Lupton, 1976; Honda *et al.*, 1991). Unlike the other noble gases, neon cannot be subducted in the Earth's interior (Hiyagon, 1994). Thus it is not possible to dilute the original trapped gas with highly fractionated atmospheric neon. The record of original emplacement is preserved.

If neon, which diffuses so easily through solids, was retained by the Earth's rocks from the time of the planet's accretion, we can reasonably assume that some water was also kept in the interior, to emerge after the catastrophic formation of the moon, mixing with incoming water from comets to form the oceans we find today. This perspective supports the idea that we may yet find evidence of this original water with $D/H < \text{SMOW}$ in mantle-derived rocks on Mars.

Returning to the Earth, it appears that the atmospheric neon bears a record of an early fractionating process that sharply reduced the ratio of $^{20}\text{Ne}/^{22}\text{Ne}$ from the solar value. This process must have affected all of the other species in the atmosphere at the time. It may have been the massive, hydrodynamic escape of hydrogen produced by the reduction of water by contemporary mantle-crustal iron (Dreibus and Wänke, 1989; Pepin, 1991). The fact that we do not see evidence of such a fractionation in atmospheric nitrogen today suggests that the nitrogen we breathe reached the Earth after the vigorous escape process had ended. Cometary delivery of nitrogen (and other volatiles) *but not neon* offers an easy means of achieving this situation, but we need more measurements of $^{14}\text{N}/^{15}\text{N}$ in other molecules in comets to be certain. The only cometary measurement of nitrogen isotopes we have refers to HCN, which is a trace constituent ($<1\%$) in cometary nuclei (Crovisier, 1998). We need to know the average value of the isotope ratio in **all** cometary N-compounds to see how closely cometary nitrogen comes to the gas we breathe on Earth. It may well be that neon is a kind of atmospheric fossil, a remnant of conditions that existed on the Earth before the volatiles that produced the bulk of the present atmosphere were in place.

What about Venus? The atmosphere of this planet contains 21 ± 5 times the amount of neon found on Earth (Donahue and Pollack, 1983). Perhaps the grains that formed Venus simply accumulated more solar wind neon than the Earth, because of their greater proximity to the sun (Wetherill, 1981). Perhaps both planets started with the same neon content, but less neon escaped from Venus. This would be consistent with the higher value of $^{20}\text{Ne}/^{22}\text{Ne} = 11.8 \pm 0.7$ measured on Venus by Istomin *et al.* (1982) compared with 9.8 on Earth.

On the other hand we have argued above that the heavy noble gases were delivered to Venus by icy planetesimals that condensed at temperatures of about 30 K or less. In this case, there is the possibility that these same objects could have delivered some neon. For example, ice forming at $T = 23 \pm 3$ K can trap $\sim 3\%$ of the ambient neon gas, while trapping all of the available Ar, Kr and Xe. Fractionation of this amount of neon by escape could reduce the initial planetesimal-delivered value of $\text{Ne}/\text{Ar} = 1$ to the present value of 0.25 ± 0.10 while changing the isotope

ratio from 13.8 to the value of 11.8 ± 0.7 reported by Istomin *et al.* (1982). Other scenarios are certainly possible, including the baseline case of no neon loss and no isotope fractionation. The latter would be accommodated by the results of Hoffman *et al.* (1980), who reported a value of $^{20}\text{Ne}/^{22}\text{Ne} = 14 (+6/-3)$ for this difficult measurement. It is obviously important to derive more precise values for both the abundance and the isotope ratio of neon on Venus to determine the origin and history of this gas on the planet.

Note that even with icy planetesimals delivery of neon to Venus, the maximum amount of nitrogen these low temperature comets could deliver would be only 30 times the argon abundance, still approximately 30 times less than the abundance of nitrogen we find in the planet's present atmosphere (Hoffman *et al.*, 1980). Hence the nitrogen requires another source, which we have suggested is icy planetesimals from the Saturn-Jupiter region, as in the case of the Earth (Owen and Bar-Nun, 1995a). The best current value for $^{14}\text{N}/^{15}\text{N}$ on Venus is terrestrial $\pm 20\%$ (Hoffman *et al.*, 1979) (Figure 5L). As this isotope ratio depends on the mixing of at least two reservoirs with possible modifications through escape processes, it would be surprising to find identical values of $^{14}\text{N}/^{15}\text{N}$ on both Venus and Earth. Improving this measurement should be a major objective of any future atmospheric probes to Venus.

6. Conclusions

How unique is the Earth? This is a perennial question in efforts to estimate the possibilities for abundant life in the universe. We have argued here that the source of our planet's atmosphere can be found in a combination of volatiles trapped in the rocks that made the planet and a late-accreting veneer of volatile-rich material delivered by icy planetesimals. The volatiles composing the atmosphere include the carbon, nitrogen, and water essential to life. The question then is, how common are these rocks and ices in the galaxy? At the level of detail we need for a truly satisfactory answer, we must admit that we lack the necessary data. We can draw some confidence from the often-cited similarities between the molecules found in comets and those in interstellar clouds (e.g., Crovisier, 1998) which may lead us to expect that icy planetesimals that form in any planetary system originating from an interstellar cloud will carry these same biogenic materials. Hence this model for the origin of our planet's atmosphere suggests that there is nothing unique about the inventory of volatiles that was delivered to the Earth. Current studies of the Martian atmosphere, aided by study of the SNC meteorites, reinforce this idea by indicating a similar inventory on that planet. The explanation we have given for the anomalous noble gas abundances on Venus suggests that the same inventory is present on Venus, with just an exotic 'spike' of gases captured by a special family of icy planetesimals that formed at low temperatures. Based on what we know

today, it appears that Oro's (1961) original insight probably applies throughout the galaxy.

Nevertheless, we are still in the stage of finding 'similarities' and 'indications'. We are far from a rigorous proof of the validity of the icy impact model. We have stressed the boundary conditions provided by the abundances and isotope ratios of the noble gases and determinations of cometary D/H. As we have seen, these boundary conditions are blurred by the effects of atmospheric escape and contributions from multiple molecular reservoirs. It is clear that meteoritic delivery of volatiles cannot by itself satisfy the constraints set by our present knowledge of noble gas abundances and isotope ratios. However, the cometary alternative that we have emphasized will remain conjectural until noble gases are actually measured in several comets. Although laboratory studies strongly suggest that comets can deliver the correct *elemental* abundances, we have not yet found evidence that trapping of gas in ice affects the relative abundance of Xe isotopes (Notesco *et al.*, 1999). The sensitivity of these experiments needs to be improved and future work should include a test of multiple sublimation and deposition events. In the absence of such evidence, we are forced to assume that comets carry xenon whose isotopes resemble the distribution found in the terrestrial and Martian atmospheres rather than that found in the solar wind. It is not at all obvious why this should be the case, although the existence of several different types of xenon in the solar system (e.g., Swindle, 1988; Zahnle, 1993; Pepin, 1994a) allows this possibility to be taken seriously. If the cometary xenon in fact resembles solar wind xenon, it will be necessary to invoke a fractionating process that acted to produce identical results for xenon on Mars and Earth followed by subsequent, selected replacement of other volatiles, as developed and described in detail by Pepin (1991, 1994b, 1997).

The xenon isotopes provide the best test of a cometary connection, as the isotopes of less massive species are more easily fractionated by atmospheric processes and similarities in elemental abundances can always be attributed to coincidence. Nevertheless, it is important not to lose sight of other key volatiles, particularly nitrogen.

How can we move forward from this unsatisfactory situation? There are a number of possible sources of new data on the horizon:

1. MARS. The Japanese Nozomi Mission launched in 1998 carries instruments that will teach us much more about possible non-thermal escape processes on Mars. This knowledge will allow a more confident reconstruction of the early mass and composition of the Martian atmosphere. These parameters can then be used (again!) to test our understanding of the origin of our own atmosphere. Mars Express, an ESA mission to be launched in 2003, will include a mass spectrometer that will re-analyze the neutral atmosphere.

If present plans mature, the steps forward achieved by Nozomi and Mars Express will soon be overshadowed by information obtained from Mars Sample Return Missions, scheduled to begin in 2011. These missions will bring back samples

of Martian rocks and atmosphere for analysis on Earth, enabling far more accurate measurements of isotopic ratios than we can expect from missions to the planet. These investigations will include not only the noble gases, but also isotopes of carbon, nitrogen, and oxygen, the last in both H₂O and CO₂. With the kind of precision obtainable in laboratories on Earth, great progress should be achieved in unraveling the history of the Martian atmosphere from these isotope measurements, including estimates of the sizes and locations of contemporary reservoirs of H₂O and CO₂ (McElroy *et al.*, 1977; Owen *et al.*, 1988; Jakosky, 1991; Owen, 1992; Jakosky *et al.*, 1994). Another goal of this research should be a search for low values of D/H in water from mantle-derived rocks, which should also contain neon with ²⁰Ne/²²Ne approaching the solar value of 13.8.

2. COMETS. Both NASA and ESA are planning missions that will rendezvous with short period comets originating from the Kuiper Belt. These missions will have the capability to detect and measure the abundances of the heavy noble gases and their isotopes and to investigate isotope ratios of nitrogen in various compounds. It is especially important to have this information from several comets. We already know that the composition of comets can vary, both from the laboratory work on the trapping of gas in ice (Figure 3) and from observations of variations in the abundances of carbon compounds in comets (Fink, 1992; A'Hearn *et al.*, 1995).

The ESA rendezvous mission to Comet Wirtanen is called *Rosetta*, it should arrive at its destination in 2012. The first NASA comet mission is called *Deep Space 1* (DS-1), a technology-testing mission that uses an ion engine for continuous thrusting and is currently (March 2001) on track to encounter Comet Borrelly in September 2001. DS-1 will be followed by the CONTOUR mission, scheduled to launch in 2002 and designed to fly past three comets starting with P/Encke in 2003. While these missions will provide a major advance over our present state of knowledge, we will ultimately need returned samples to get the level of precision we want, just as in the case of Mars. A comet sample-return mission is not yet under serious consideration by any Space Agency.

There is hope for an inexpensive atmospheric probe to Venus within the next decade, which would tell us more about the nitrogen isotopes and the anomalous abundances of the noble gases and their isotopes on our sister planet. We will await all these new results with great interest.

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References

- A'Hearn, M., Millis, R. L., Schleicher, J. D. and Birch, P. V.: 1995, The ensemble properties of comets: Results from narrowband photometry of 85 comets, 1976–1992, *Icarus* **1881**, 223–270.
- Anders, E. and Grevesse, N.: 1989, Abundances of the elements: Meteoritic and solar, *Geochim. Cosmochim. Acta* **53**, 197–214.
- Anders, E. and Owen, T.: 1977, Mars and Earth: Origin and abundances of volatiles, *Science* **198**, 453–465.
- Bar-Nun, A., Herman, B., Laufer, D. and Rappoport, M. L.: 1985, Trapping and release of gases by water ice and implications for icy bodies, *Icarus* **63**, 317–332.
- Bar-Nun, A., Kleinfeld, I. and Kochavi, E.: 1988, Trapping of gas mixtures by amorphous water ice, *Phys. Rev. B* **38**, 7749–7754.
- Balsiger, H., Altwegg, K. and Geiss, J.: 1995, D/H and $^{18}\text{O}/^{16}\text{O}$ ratio in the hydronium ion and in neutral water from in situ ion measurements in Comet P/Halley, *J. Geophys. Res.* **100**, 5827–5834.
- Becker, R. H. and Pepin, R. O.: 1984, The case for a Martian origin of the Shergottites: Nitrogen and noble gases in EETA 79001, *Earth Planet. Sci. Lett.* **69**, 225–242.
- Becker, R. H. and Pepin, R. O.: 1993, Nitrogen and noble gases in a glass sample from Lew 88516., (Abstracts) In *Lunar and Planetary Science Conference XXIV*, pp. 77–78. Lunar and Planetary Institute, Houston.
- Bernatowicz, T. J., Kennedy, B. M. and Podosek, F. A.: 1985, Xe in glacial ice and the atmospheric inventory of noble gases, *Geochim. Cosmochim. Acta* **49**, 2561–2564.
- Bockelee-Morvan, D., Gautier, D., Lis, D. C., Young, D., Keene, J., Phillips, T. G., Owen, T., Crovisier, J., Goldsmith, P. F., Bergin, E. A., Despois, D. and Wooten: 1998, Deuterated water in comet C/1996 B2 (Hyakutake) and its implications for the origin of comets, *Icarus* **133**, 147–162.
- Bogard, D. D. and Garrison, D. H.: 1998, Relative abundances of argon, krypton and xenon in the Martian atmosphere as measured in Martian meteorites, *Geochim. Cosmochim. Acta* **62**, 1829–1835.
- Bogard, D. D., Hörz, F. and Johnson, P. H.: 1986, Shock-implanted noble gases: An experimental study with implications for the origin of Martian gases in Shergottite meteorites, Proc. Lunar and Planet Sci. Conf. 17th, *J. Geophys. Res. (Suppl.)* **91**, E99-E114.
- Bogard, D. D. and Johnson, P. H.: 1983, Martian gases in an Antarctic meteorite?, *Science* **221**, 651–654.
- Carr, M. H.: 1986, Mars: A water-rich planet?, *Icarus* **56**, 187–216.
- Carr, M. H. and Wänke, U.: 1992, Earth and Mars: Water inventories as clues to accretional histories, *Icarus* **98**, 61–71.
- Chick, K. M. and Cassen, P.: 1997, Thermal processing of interstellar dust grains in the primitive solar environment, *Astrophys. J.* **447**, 398–409.
- Chin, Y.-N., Henkel, C., Langer, N. and Mauersberger, R.: 1999, The detection of extragalactic ^{15}N : Consequences for nitrogen nucleosynthesis and chemical evolution, *Astrophys. J. Lett.* **512**, L143–L146.
- Chyba, A. C.: 1990, Impact delivery and erosion of planetary oceans in the inner solar system, *Nature* **343**, 129–133.
- Chyba, C., Owen, T. and Ip, W.-H.: 1994, Impact delivery of volatiles and organic molecules to Earth, in *Hazards Due to Comets and Asteroids*, (T. Gehrels, ed.) pp. 49–58, U. of Arizona Press, Tucson.
- Coustenis, A.: 1999, Private communication about D/H on Titan from ISO observations – analysis in progress.
- Craig, H. and Lupton, J. E.: 1976, Primordial neon, helium and hydrogen in oceanic basalts, *Earth Planet. Sci. Lett.* **31**, 369–385.
- Crovisier, J.: 1998, Physics and chemistry of comets: Recent results from comets Hyakutake and Hale-Bopp. Answers to old questions and new enigmas, *Faraday Discussions* **109**, 437–452.

- Crovisier, J. D., Leech, K., Bockelee-Morvan, D., Brooke, T. Y., Hanner, M. S., Altieri, B., Keller, H. U. and Lellouch, E.: 1997, The spectrum of comet Hale-Bopp (C/1995 01) observed with the Infrared Space Observatory at 2.9 astronomical units from the sun, *Science* **275**, 1904–1907.
- Dahmen, G., Wilson, T. L. and Matteucci, F.: 1995, The nitrogen isotope abundance in the galaxy, *Astron. Astrophys.* **295**, 194–198.
- Davies, J. K., Roush, T. L., Cruikshank, D. P., Bartholomew, M. J., Geballe, T. R., Owen, T. and de Bergh, C.: 1997, The detection of water ice in comet Hale-Bopp, *Icarus* **127**, 238–245.
- Delsemme, A.: 1991, Nature and history of the organic compounds in comets: An astrophysical view, in R. L. Newburn, Jr., M. Neugebauer and J. Rahe (eds), *Comets in Post-Halley Era*, pp 417–428, Kluwer, Dordrecht.
- Delsemme, A. H.: 2000, 1999 Kuiper Prize Lecture: Cometary origin of the biosphere, *Icarus* **146**, 313–325.
- Donahue, T. M. and Pollack, J. B.: 1983, Origin and evolution of the atmosphere of Venus, in D. M. Hunten, L. Colin, T. M. Donahue and V. I. Moroz (eds), *Venus*, pp 1003–1036, U. of Arizona Press, Tucson.
- Drake, M. J., Swindle, T. D., Owen, T. and Musselwhite, D. L.: 1994, Fractionated martian atmosphere in the Nakhilites?, *Meteoritics* **29**, 854–859.
- Dreibus, G. and Wänke, W.: 1989, Supply and loss of volatile constituents during the accretion of terrestrial planets, in S. K. Atreya, J. P. Pollack, and M. S. Matthews (eds), *Origin and Evolution of Planetary and Satellite Atmospheres*, pp 268–288, U. of Arizona Press, Tucson.
- Eberhardt, P. M., Reber, D., Krankowsky, D. and Hodges, R. R.: 1995, The D/H and $^{18}\text{O}/^{16}\text{O}$ ratios in water from Comet P/Halley, *Astron. Astrophys.* **302**, 301–316.
- Feuchtgruber, H., Lellouch, E., Bézard, B., Encrenaz, Th., de Graaw, Th. and Davis, G. R.: 1999, Detection of HD in the atmospheres of Uranus and Neptune: A new determination of the D/H ratios, *Astron. Astrophys.* **341**, 17–21.
- Fink, U.: 1992, Comet Yanaka (1998r) A new class of carbon poor comet, *Science* **257**, 1926–1929.
- Fouchet, T., Lellouch, E., Bézard, B., Encrenaz, T., Drossart, P., Feuchtgrubert, H. and de Graauw, T.: 2000, ISO-SWS observations of Jupiter: Measurement of the ammonia tropospheric profile and of the $^{15}\text{N}/^{14}\text{N}$ isotopic ratio, *Icarus* **143**, 223–243.
- Garrison, D. H. and Bogard, D. S.: 1998, Isotopic composition of trapped and cosmogenic noble gases in several Martian meteorites, *Meteoritics* **33**, 721–736.
- Geiss, J.: 1988, Composition of Halley's comet: Clues to origin and history of cometary matter, *Rev. Mod. Astron.* **1**, 1–27.
- Greely, R.: 1987, Release of juvenile water on Mars: Estimated amounts and timing associated with volcanism, *Science* **136**, 688–690.
- Halley, E.: 1687, As referenced in *Comets, Popular Culture and the Birth of Modern Cosmology*, by S. S. Genuth, p. 162, Princeton University Press, Princeton.
- Hashizume, K., Chaussidan, M. and Marty, B.: 2000, Nitrogen isotope analysis of lunar regolith using an ion microprobe-search of the solar wind component. *Lunar and Planetary Science XXXI* (abs.) 1565.
- Hiyagon, H.: 1994, Retention of solar helium and neon in IDPs in deep sea sediment, *Science* **263**, 1257–1259.
- Hoffman, J. H., Hodges, R. R., Jr., McElroy, M. B., Donahue, T. M. and Kolpin, M.: 1979, Composition and structure of the Venus atmosphere: Results from Pioneer Venus, *Science* **205**, 49–52.
- Hoffman, J. H., Oyama, V. I. and von Zahn, U.: 1980, Measurements of the Venus lower atmosphere composition: A comparison of results, *J. Geophys. Res.* **85**, 7871–7881.
- Honda, M., McDougall, I., Patterson, D., Douglaris, A. and Clague, D. A.: 1991, Possible solar noble-gas component in Hawaiian basalts, *Nature* **349**, 149–151.
- Hunten, D. M., Pepin, R. O. and Owen, T. C.: 1988, Planetary atmospheres, in J. F. Kerridge and M. S. Matthews (eds), *Meteorites*, pp. 565–591, U. of Arizona Press, Tucson.

- Istomin, V. G., Grechnev, K. V. and Kochnev, V. A.: 1982, Preliminary results of mass-spectrometric measurements on board the Venera 13 and Venera 14 probe, *Pisma Astron. Zh.* **8**, 391–398.
- Jakosky, B. M.: 1991, Mars volatile evolution: Evidence from stable isotopes, *Icarus* **94**, 14–31.
- Jakosky, B. M., Pepin, R. J., Johnson, R. E. and Fox, J. L.: 1994, Mars atmospheric loss and isotopic fractionation by solar-wind induced sputtering and photochemical escape, *Icarus* **111**, 271–288.
- Jewitt, D. C., Matthews, H. E., Owen, T. and Meier, R.: 1997, Measurements of $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$ and $^{32}\text{S}/^{34}\text{S}$ ratios in comet Hale-Bopp (C/1995 01), *Science* **278**, 90–93.
- Kallenbach, R., Geiss, J., Ipavich, F. M., Gloeckler, G., Bochsler, P., Gliem, F., Hefti, S., Hilchenbach, M. and Hovestadt, D.: 1998, Isotopic composition of solar wind nitrogen: First *in situ* determination with CELIAS/MTOF spectrometer on board SOHO, *Astrophys. J. Lett.* **507**, L185–L188.
- Karlsson, H. R., Clayton, R. N., Gibson, Jr., E. K. and Mayeda, T. K.: 1992, Water in SNC meteorites: Evidence for a martian hydrosphere, *Science* **255**, 1409–1411.
- Krankowsky, D.: 1991, 'The Composition of Comets', in R. L. Newburn, Jr. and M. Neugebauer, J. Rahe (eds), *Comets in the Post-Halley Era*, pp. 855–879, Kluwer, Dordrecht.
- Krasnopolsky, V. A., Mumma, M. J., Abbott, M., Flynn, B. C., Meech, K. J., Yeomans, D. K., Feldman, P. O. and Cosmovici, C. B.: 1997a, High resolution spectroscopy of Mars at 3.7 and 8 μm : A sensitive search for H_2 , O_2 , H_2CO , HCl and CH_4 , and detection of HDO, *J. Geophys. Res.* **102**, 6524–6534.
- Krasnopolsky, V. A., Mumma, M. J., Abbott, M., Flynn, B. C., Meech, K. J., Yeomans, D. K., Feldman, P. D. and Cosmovici, C. B.: 1997b, Detection of soft x-rays and a sensitive search for noble gases in comet Hale-Bopp (C/1995 01), *Science* **277**, 1488.
- Laufer, D., Kochavi, E. and Bar-Nun, A.: 1987, Structure and dynamics of amorphous water ice, *Phys. Rev. B.* **36**, 9219–9227.
- Lécluse, C. and Robert, F.: 1994, Hydrogen isotope exchange rates: Origin of water in the inner solar system, *Geochim. Cosmochim. Acta.* **58**, 2297–2339.
- Leshin, L. A., Epstein, S. and Stolpher, E. M.: 1996, Hydrogen isotope geochemistry of SNC meteorites, *Geochim. Cosmochim. Acta.* **60**, 2635–2650.
- Linsky, J. L.: 1996, GHRS observations of the LISM, *Space Sci Rev* **78**, 157–164.
- Lunine, J. L., Engel, S., Rizk, B. and Horanyi, M.: 1991, Sublimation and reformation of icy grains in the primitive solar nebula, *Icarus* **94**, 333–343.
- Mahaffy, P. R., Donahue, T. M., Atreya, S. K., Owen, T. C. and Niemann, H. B.: 1998, Galileo Probe Measurements of D/H and $^3\text{He}/^4\text{He}$ in Jupiter's atmosphere, in N. Prantzos, M. Tosi and R. von Steiger (eds), *Primordial Nuclei and Their Evolution*, pp. 251–264, Kluwer, Dordrecht.
- Marti, K., Kim, J. S., Thakur, A. N., McCoy, T. J. and Keil, K.: 1995, Signatures of the martian atmosphere in glass of the Zagami meteorite, *Science* **267**, 1981–1984.
- Mathew, K. J., Kim, J. S. and Marti, K.: 1998, Martian atmospheric and indigenous components of xenon and nitrogen in the Shergotty, Nakhla and Chassigny group meteorites, *Meteorites and Planet Sci.* **33**, 655–664.
- Mathew, K. J. and Marti, K.: 2001, Early evolution of Martian volatiles: Nitrogen and noble gas components in ALH 84001 and Chassigny, *J. Geophys. Res.* **106**, 1401–1422.
- McElroy, M. B., Kong, T. Y. and Yung, Y. L.: 1977, Photochemistry and evolution of Mars atmosphere: A Viking perspective, *J. Geophys. Res.* **82**, 4379–4388.
- McSween, H. Y., Jr.: 1994, What have we learned about Mars from SNC meteorites?, *Meteoritics* **29**, 757–779.
- Meier, R. and Owen, T.: 1999, Deuterium in comets, in K. Altwegg, P. Ehrenfreund, J. Geiss and H. Huebener (eds), *Composition and Origin of Cometary Materials*, pp. 33–34, Kluwer, Dordrecht.
- Meier, R., Owen, T. C., Matthews, H. E., Senay, M., Biver, N., Bockelée-Morvan, D., Crovisier, J. and Gautier, D.: 1998b, Deuterium in Comet C/1995 01 (Hale-Bopp): Detection of DCN, *Science* **279**, 1707–1710.

- Meier, R., Owen, T. C., Matthews, H. E., Jewitt, D., Bockelée-Morvan, D., Biver, N., Crovisier, J. and Gautier, D.: 1998a, A determination of the HDO/H₂O ratio in Comet C/1995 01 (Hale Bopp), *Science* **279**, 842–844.
- Melosh, H. J. and Vickery, A. M.: 1989, Impact erosion of the primordial atmosphere of Mars, *Nature* **388**, 487–489.
- Millar, T. J., Bennett, A. and Herbst, E.: 1989, Deuterium fractionation in dense interstellar clouds, *Astrophys. J.* **340**, 906–920.
- Mumma, M. J., Weissman, P. R. and Stern, S. A.: 1993, Comets and the origin of the solar system: Reading the Rosetta Stone, in E. H. Levy, J. I. Lunine and M. S. Matthews (eds), *Protostars and Planets III*, pp 1177–1252, University of Arizona Press, Tucson.
- Musselwhite, D. M., Drake, M. J. and Swindle, T. O.: 1991, Early outgassing of Mars supported by differential water solubility of iodine and xenon, *Nature* **352**, 697–699.
- Nier, A. O. and McElroy, M. B.: 1977, Composition and structure of Mars upper atmosphere: Results from the neutral mass spectrometers on Viking 1 and 2, *J. Geophys. Res.* **82**, 4341–4350.
- Notesco, G. and Bar-Nun, A.: 1996, Enrichment of CO over N₂ by their trapping in amorphous ice and implications to Comet Halley, *Icarus* **122**, 118–121.
- Notesco, G., Laufer, D., Bar-Nun, A. and Owen, T.: 1999, An experimental study of the isotopic enrichment in Ar, Kr and Xe when trapped in water ice, *Icarus* **142**, 298–300.
- Nuth, J. A. III, Hill, H. G. M. and Kletetschka, G.: 2000, Determining the ages of comets from the fraction of crystalline dust, *Nature* **406**, 275–276.
- Oro, J.: 1961, Comets and the formation of biochemical compounds on the primitive Earth, *Nature* **190**, 389–390.
- Ott, U.: 1988, Noble gases in SNC meteorites: Shergotty, Nakhla, Chassigny, *Geochim. Cosmochim. Acta.* **52**, 1937–1948.
- Ott, U. and Begemann, F.: 1985, Are all the martian meteorites from Mars?, *Nature* **317**, 509–512.
- Ott, U., Löhr, H. P. and Begemann, F.: 1988, New noble gas data from SNC meteorites: Zagami, Lafayette and etched Nakhla, *Meteoritics* **23**, 295–296.
- Owen, T.: 1992, The composition and early history of the atmosphere of Mars, in H. H. Kieffer, B. M. Jakosky, C. W. Snyder, and M. S. Matthews (eds), *Mars*, pp 818–834, U. of Arizona Press, Tucson.
- Owen, T. and Bar-Nun, A.: 1993, Noble gases in atmospheres. *Nature* **361**, 693–694.
- Owen, T. and Bar-Nun, A.: 1995a, Comets, impacts and atmospheres, *Icarus* **116**, 215–226.
- Owen, T. and Bar-Nun, A.: 1995b, Comets, impacts and atmospheres II, Isotopes and noble gases, in K. Farley (ed.), *Volatiles in the Earth and Solar System*, pp 123–138, *AIP Conf. Proc.* **341**, 123–138.
- Owen, T. and Bar-Nun, A.: 2001, (in preparation).
- Owen, T., Bar-Nun, A. and Kleinfeld, I.: 1991, Noble gases in terrestrial planets: Evidence for cometary impacts, in R. L. Newburn, Jr., M. Neugebauer and J. Rahe (eds), *Comets in the Post-Halley Era*, pp 429–438, Kluwer, Dordrecht.
- Owen, T., Bar-Nun, A. and Kleinfeld, I.: 1992, Possible cometary origin of heavy noble gases in the atmospheres of Venus, Earth and Mars, *Nature* **358**, 43–46.
- Owen, T., Biemann, K., Rushneck, D. R., Biller, J. E., Howarth, D. W. and Lafleur, A. L.: 1977, The composition of the atmosphere at the surface of Mars, *J. Geophys. Res.* **82**, 4635–4639.
- Owen, T., Mahaffy, P., Niemann, H. B., Atreya, S., Donohue, T., Bar-Nun, A. and de Pater, I.: 1999, A low-temperature origin for the planetesimals that formed Jupiter, *Nature* **402**, 269–270.
- Owen, T., Mahaffy, P., Niemann, H., Atreya, S. and Wong, M.: 2001, Proto-solar nitrogen, *Astrophys. J. Lett.* **553**, L77–L79.
- Owen, T., Maillard, J. P., de Bergh, C. and Lutz, B. L.: 1988, Deuterium on Mars: The abundance of HDO and the value of D/H, *Science* **240**, 1767–1770.
- Ozima, M. and Wada, N.: 1993, Noble gases in atmospheres, *Nature* **361**, 693.

- Ozima, M., Wieler, R., Marty, B. and Podosek, F. A.: 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.
- Pavlov, A. A., Pavlov, A. K. and Kasting, J. F.: 1999, Irradiated planetary dust particles as a possible solution for the deuterium/hydrogen paradox of Earth's oceans, *J. Geophys. Res.* **104**, 30725–30728.
- Pepin, R. O.: 1989, Atmospheric compositions: Key similarities and differences, in S. K. Atreya, J. B. Pollack and M. S. Matthews (eds), *Origin and Evolution of Planetary and Satellite Atmospheres*, pp 293–305, U. of Arizona Press, Tucson.
- Pepin, R. O.: 1991, On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles, *Icarus* **92**, 2–79.
- Pepin, R. O.: 1994a, The hunt for U-Xenon, *Meteoritics* **29**, 568–569.
- Pepin, R. O.: 1994b, Evolution of Earth's noble gases: Consequences of assuming hydrodynamic loss driven by giant impact, *Icarus* **126**, 148–156.
- Pollack, J. B.: 1979, Climatic change on the terrestrial planets, *Icarus* **37**, 479–553.
- Robert, F.: 1997, Paper presented at Blois Symposium: The Solar System: The Longview (Proceedings volume in press, ed. L. Celniker, T. Van).
- Robert, R., Rejon-Michel, and Javoy, M.: 1992, Oxygen isotopic homogeneity of the Earth: New evidence, *Earth and Planet Sci. Lett.* **108**, 1–9.
- Sill, G. T. and Wilkening, L.: 1978, Ice clathrate as a possible source of the atmospheres of the terrestrial planets, *Icarus* **33**, 13–27.
- Swindle, T. D.: 1988, Trapped noble gases in meteorites, in J. F. Kerridge and M. S. Matthews (eds), *Meteorites*, pp 535–564, U. of Arizona Press, Tucson.
- Swindle, T. D., Caffee, M. W. and Hohenberg, C. M.: 1986, Xenon and other noble gases in shergottites, *Geochim. Cosmochim. Acta* **50**, 1001–1015.
- Terzieva, R. and Herbst, E.: 2000, The possibility of nitrogen isotopic fractionation in interstellar clouds, *Mon. Not. Roy. Astron. Soc* **317**, 563–568.
- Turekian, K. K. and Clark, Jr., S. P.: 1975, The non-homogeneous accumulation model for terrestrial planet formation and the consequences for the atmosphere of Venus, *J. Atmos. Sci.* **32**, 1257–1261.
- Van Dishoeck, E. V., Blake, G. A., Draine, B. T. and Lunine, J. I.: 1993, in E. H. Levy and J. I. Lunine (eds), *Protostars and Planets III*, pp 163–244, U. of Arizona Press, Tucson.
- Wacker, J. F. and Anders, E.: 1984, Trapping of xenon in ice and implications for the origin of the Earth's noble gases, *Geochim. Cosmochim. Acta* **48**, 2372–2380.
- Watson, L. L., Hutcheon, I. D. and Stolper, E. M.: 1994, Water on Mars: Clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites, *Science* **265**, 86–90.
- Wetherill, G.: 1981, Solar wind origin of ^{36}Ar on Venus, *Icarus* **46**, 70–80.
- Wilson, T. L. and Rood, R. T.: 1994, Abundances in the interstellar medium, *Ann. Rev. Astron. Astrophys.* **32**, 191–226.
- Yung, Y. and Dissly, R. W.: 1992, Deuterium in the Solar System, in J. A. Kaye (ed.), *Isotope Effects in Gas-Phase Chemistry*, p 369–389, American Chemical Society Symposium Series, No. 502.
- Zahnle, K.: 1993, Planetary noble gases, in E. H. Levy and J. I. Lunine (eds), *Protostars and Planets III*, pp 1305–1338, U. of Arizona Press, Tucson.
- Zahnle, K., Kasting, J. E. and Pollack, J. B.: 1990, Mass fractionation of noble gases in diffusion-limited hydrodynamic hydrogen escape, *Icarus* **84**, 502–527.