MARTIAN VOLATILES: ISOTOPIC COMPOSITION, ORIGIN, AND EVOLUTION

D.D. BOGARD[1], R. N. CLAYTON[2], K. MARTI[3], T. OWEN[4] and G. TURNER[5]

[1]*Planetary Sciences SN, NASA Johnson Space Center, Houston, TX 77058, USA*
[2]*Enrico Fermi Institute, University of Chicago, 5640 S. Ellis, Chicago, IL 60637, USA*
[3]*Chemistry Department, University of California San Diego, La Jolla, CA 92093-0317, USA*
[4]*Institute for Astronomy, 2680 Woodlawn Dr., University of Hawaii, Honolulu, HI 96822, USA*
[5]*Department of Earth Sciences, University of Manchester M13 9PL, UK*

Abstract. Information about the composition of volatiles in the Martian atmosphere and interior derives from Viking spacecraft and ground-based measurements, and especially from measurements of volatiles trapped in Martian meteorites, which contain several distinct components. One volatile component, found in impact glass in some shergottites, gives the most precise measurement to date of the composition of Martian atmospheric Ar, Kr, and Xe, and also contains significant amounts of atmospheric nitrogen showing elevated $^{15}N/^{14}N$. Compared to Viking analyses, the $^{36}Ar/^{132}Xe$ and $^{84}Kr/^{132}Xe$ elemental ratios are larger in shergottites, the $^{129}Xe/^{132}Xe$ ratio is similar, and the $^{40}Ar/^{36}Ar$ and $^{36}Ar/^{38}Ar$ ratios are smaller. The isotopic composition of atmospheric Kr is very similar to solar Kr, whereas the isotopes of atmospheric Xe have been strongly mass fractionated in favor of heavier isotopes. The nakhlites and ALH84001 contain an atmospheric component elementally fractionated relative to the recent atmospheric component observed in shergottites. Several Martian meteorites also contain one or more Martian interior components that do not show the mass fractionation observed in atmospheric noble gases and nitrogen. The D/H ratio in the atmosphere is strongly mass fractionated, but meteorites contain a distinct Martian interior hydrogen component. The isotopic composition of Martian atmospheric carbon and oxygen have not been precisely measured, but these elements in meteorites appear to show much less variation in isotopic composition, presumably in part because of buffering of the atmospheric component by larger condensed reservoirs. However, differences in the oxygen isotopic composition between meteorite silicate minerals (on the one hand) and water and carbonates indicate a lack of recycling of these volatiles through the interior. Many models have been presented to explain the observed isotopic fractionation in Martian atmospheric N, H, and noble gases in terms of partial loss of the planetary atmosphere, either very early in Martian history, or over extended geological time. The number of variables in these models is large, and we cannot be certain of their detailed applicability. Evolutionary data based on the radiogenic isotopes (i.e., $^{40}Ar/^{36}Ar$, $^{129}Xe/^{132}Xe$, and $^{136}Xe/^{132}Xe$ ratios) are potentially important, but meteorite data do not yet permit their use in detailed chronologies. The sources of Mars' original volatiles are not well defined. Some Martian components require a solar-like isotopic composition, whereas volatiles other than the noble gases (C, N, and H_2O) may have been largely contributed by a carbonaceous (or cometary) veneer late in planet formation. Also, carbonaceous material may have been the source of moderate amounts of water early in Martian history.

1. Introduction

Very early telescopic observations of Mars revealed polar caps whose waxing and waning with the seasons were interpreted as evidence that they were made of volatiles condensed from the atmosphere. As late as 1950, by analogy to Earth, it was generally assumed that the Martian atmosphere consisted mainly of nitrogen and Ar. In 1952, strong absorption bands of CO_2 were reported, and for two decades this was the only detected component of the Martian atmosphere. As early as the 1920s it was estimated that the atmospheric pressure at the Martian surface is no more than a few percent that of the Earth's pressure, but for decades our knowledge of the actual pressure did not improve. Significant advancement of information about Mars and its atmosphere came with the Mariner spacecraft flybys in the 1960s and the Viking missions in 1976. Another major advancement occurred in the early 1980s with the realization that we had meteorites from Mars in our collections, and that these contained Martian volatiles. (See e.g., Kieffer *et al.*, 1992, for a historical discussion of Mars studies.)

2. Atmospheric Composition

2.1. VIKING MEASUREMENTS

The first detailed measurement of the composition of the Martian atmosphere was made using mass spectrometers on the two Viking landers (Owen *et al.*, 1977; Nier and McElroy, 1977; Owen, 1992). In addition to consisting of ∼95% CO_2 and variable amounts of H_2O, the Martian atmosphere was found to contain 2.7% N_2, 1.6% Ar, 0.13% O_2, 2.5 ppm Ne, 0.3 ppm Kr, 0.08 ppm Xe, and trace amounts of other chemically reactive species. One of the more interesting observations made by Viking was an ∼62% enrichment in the $^{15}N/^{14}N$ isotopic ratio compared to the terrestrial ratio. Such large ^{15}N enrichment implies that considerable amounts of N_2 have been lost from the planet over time by a mass fractionating process, which enriches the atmospheric residue in the heavier isotope. It was estimated that approximately 99% of the original atmospheric N_2 may have been lost (McElroy *et al.*, 1977).

The Viking measurements also produced interesting data for the abundances and isotopic ratios of noble gases in the Martian atmosphere. Although the atmospheric pressure on Mars (∼6 millibars, depending on elevation) is less than 1% that of the Earth, the relative abundances of Ne, Ar, Kr, and Xe are similar to those in the Earth's atmosphere. This abundance pattern is distinct in detail from solar gases and noble gases trapped in primitive meteorites (e.g. Pepin, 1991). The specific reason for this similarity in relative noble gas abundances between the Earth and Mars is not understood. In addition to elemental abundances, the Viking instruments also measured $^{40}Ar/^{36}Ar \cong 3000 \pm 500$ and $^{129}Xe/^{132}Xe \cong 2.5\ (^{+2}_{-1})$, compared to the

TABLE I

Isotopic Determinations of Some Martian Volatiles. Data listed as "ratio" are as measured. Other ratios are given as deviations (% or ‰) relative to the standard indicated (terrestrial or solar), and values are positive except where noted as negative. The four columns of data represent the atmospheric composition as measured by Viking (Owen *et al.*, 1977; Nier and McElroy, 1977); the atmospheric compositions measured in shergottite impact glass; a possible ancient composition present in ALH84001; and the Martian interior composition as measured in Chassigny and some other SNC meteorites. See text for sources of meteorite data and additional discussion.

Isotopic Ratio	Comparison Standard	Atmos. Viking	Impact-Glass	ALH-84001	Interior SNCs
$^{36}Ar/^{132}Xe$	ratio	350^A	900 ± 100^B	~ 50	≤ 5
$^{84}Kr/^{132}Xe$	ratio	11^A	20.5 ± 1.5^B	~ 6	<1.1
$^{2}H/^{1}H$	%-terrestrial	$\sim 450^C$	$\sim 440^D$	$\sim 78^E$	~ 90
$^{15}N/^{14}N$	%-terrestrial	62 ± 16	<50	0.7	-3.0
$^{20}Ne/^{22}Ne$	ratio	n.r.	~ 10	?	?
$^{36}Ar/^{38}Ar$	ratio	5.5 ± 1.5	≤ 3.9	≥ 5	≥ 5.26
$^{40}Ar/^{36}Ar$	ratio	3000 ± 500	~ 1800	$\leq 128^F$	≤ 212
$^{86}Kr/^{84}Kr$	%-solar	n.r.	~ 0	~ 0	~ 0
$^{129}Xe/^{132}Xe$	ratio	~ 2.5	2.4–2.6	2.16	<1.07
$^{136}Xe/^{130}Xe$	%-solar	n.r.	~ 27	~ 0	~ 0
$^{13}C/^{12}C$	‰-terrestrial	0 ± 50	n.r.	~ 41	$-30/+41^G$
$^{18}O/^{16}O$	‰-terrestrial	0 ± 50	^{H}	^{H}	^{H}

A question mark indicates that the isotopic ratio is unknown. n.r. indicates that the value was not reported:

[A] Ar, Kr, and Xe elemental abundances measured by Viking were estimated to be uncertain to $\sim 20\%$, or $\sim 28\%$ in these elemental ratios, assuming uncorrelated errors.

[B] Ratios were calculated assuming atmospheric $^{129}Xe/^{132}Xe=2.6$ For a minimum atmospheric $^{129}Xe/^{132}Xe$ ratio of 2.4, these elemental ratios would be ~ 770 and ~ 18, respectively.

[C] Ground-based spectra measurement

[D] The highest $\delta D/H$ measured in Martian meteorites, 4358 ± 185‰, was found in Zagami apatite. D/H ratios apparently have not been reported for impact glass.

[E] Highest $\delta D/H$ value reported for ALH84001.

[F] Ratio may reflect either interior or ancient atmosphere components (see text).

[G] Approximate $^{13}C/^{12}C$ range measured in SNCs.

[H] The $^{17}O/^{16}O/^{18}O$ isotopic compositions in Martian meteorite silicates and water differ slightly from each other and from the Earth's values, after accounting for effects of mass fractionation produced from chemical interactions.

terrestrial atmospheric values of 296 and 0.98, respectively. Argon-40 and ^{129}Xe were formed over time by the radioactive decay of ^{40}K ($t_{1/2} = 1.28$ Gyr) and ^{129}I ($t_{1/2} = 16$ Myr), respectively, and their presence in the atmosphere is a measure of the extent of degassing of the Martian interior. Viking also measured some other isotopic ratios of atmospheric components (e.g., $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{38}Ar/^{36}Ar$) and, within relatively large measurement uncertainties, found them to resemble terrestrial values (Table I).
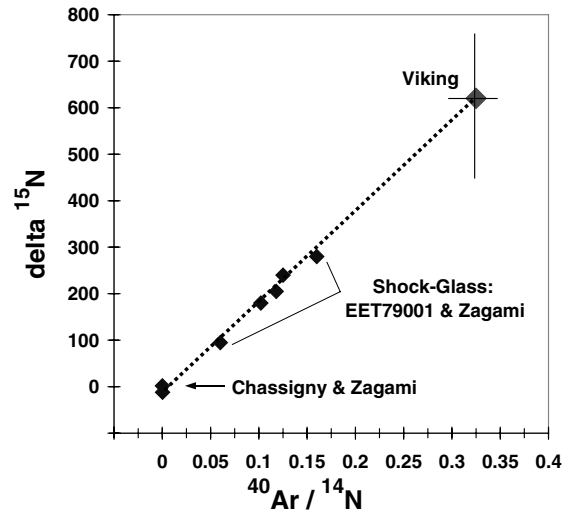
Figure 1. Values of $\delta^{15}N/^{14}N$ plotted against $^{40}Ar/^{14}N$ ratios for five samples of impact glass from the EET79001 and Zagami Martian meteorites and from bulk phases of the Chassigny and Zagami meteorites. The data indicate two-component mixing between an interior composition represented by Chassigny and the composition measured for the Martian atmosphere by Viking. Data from Owen *et al.* (1977), Becker and Pepin (1984), Marti *et al.* (1995), and Mathew and Marti (2001).

2.2. ATMOSPHERIC VOLATILES IN SNC METEORITES

A totally unexpected source of information on Martian volatiles appeared in 1983, with the recognition that impact-produced melt glass in SNC meteorite, EET79001 contained significant quantities of Martian atmospheric gases (Bogard and Johnson, 1983; Becker and Pepin, 1984). These gases were shock-incorporated into the melt when it formed by meteorite impact on the Martian surface (Bogard *et al.*, 1986; Wiens and Pepin, 1988). The presence of Martian atmospheric gases in some SNC meteorites, along with their young radiometric ages (Nyquist *et al.*, 2001) and geochemical similarity to Viking analysis of the Martian surface (McSween, 1985), became strong evidence that all of the SNC meteorites derive from Mars. Further, over the past two decades the evidence that SNC meteorites are Martian has become broader and more convincing (e.g., Treiman *et al.*, 2000), and today few workers in the field doubt their Martian origin.

Several laboratories have now measured the isotopic composition of Ne, Ar, Kr, and Xe in shock glass from several shergottite meteorites (see references in Bogard and Garrison, 1998). In addition, a significantly elevated $^{15}N/^{14}N$ ratio has been measured in shock glass from two shergottites (Wiens, 1988; Marti *et al.*, 1995; Mathew *et al.*, 1998). As shergottite shock glass can be no older than the <0.2 Gyr radiometric age of most shergottites (Nyquist *et al.*, 2001), and may well be as young as the space exposure ages of a few Myr, the gases trapped in impact glass

represent the relatively recent Martian atmosphere. For the noble gases, Martian meteorite data define the atmospheric composition to a much higher precision than do the Viking data. For N_2, however, the Martian meteorites apparently do not give the pure Martian atmospheric end member measured by Viking, but rather appear to show mixing between atmospheric N_2 and a second, much less fractionated, trapped interior component. Figure 1 plots the $\delta^{15}N$ values (deviations of the $^{15}N/^{14}N$ ratio from the terrestrial ratio, in parts per thousand) against the $^{40}Ar/^{14}N$ ratios for five shock glass samples from the EET79001 and Zagami shergottites, where both N and Ar compositions were measured in the same sample (Becker and Pepin, 1984; Marti *et al.*, 1995). Corrections were applied for cosmogenic ^{15}N and radiogenic ^{40}Ar. The data define an apparent two-component mixing trend that passes through the Martian atmospheric composition measured by Viking. Although the data trend also passes near the terrestrial composition, analyses have shown that this second volatile component in Martian meteorites is different in composition from the terrestrial component and probably is characteristic of the Martian interior. This Martian interior component is better characterized through analyses of gases in two other Martian meteorites, Chassigny and ALH84001.

These results for nitrogen can be compared to the data on H_2O in the SNCs, discussed in more detail below. Water in some SNC minerals does appear to carry the strongly fractionated hydrogen found in the atmosphere by Earth-based investigations (Owen *et al.*, 1988; Krasnopolsky *et al.*, 1997), while also carrying one or more internal components that have not experienced this fractionation (Karlsson *et al.*, 1992; Watson *et al.*, 1994; Leshin *et al.*, 1996).

2.3. Ar/Kr/Xe Relative Elemental Abundances and $^{129}Xe/^{132}Xe$

Soon after the recognition of trapped Martian atmospheric gases in shock-produced glass of shergottite meteorite EET79001, Ott and Begemann (1985) and Ott (1988) reported very different compositions for some noble gas components trapped in Martian meteorites Chassigny, Nakhla, and non-glass samples of Shergotty. The Ar/Kr/Xe elemental ratios in Chassigny in particular indicated a very large depletion of the lighter elements, relative to both solar and Martian atmospheric compositions. The isotopic composition of Xe in some Chassigny samples, however, was found to closely resemble the solar composition, including a $^{129}Xe/^{132}Xe$ ratio of ~ 1.03. The composition of trapped noble gases in bulk Shergotty was found to be intermediate to those of Chassigny and EET79001 shock-glass. These authors also noted that the lower ratio of radiogenic ^{129}Xe to trapped Xe in Chassigny and Nakhla, in comparison to trapped atmospheric gas in EET79001 glass, was opposite to the situation on Earth, where noble gases in the interior show larger $^{129}Xe/^{132}Xe$ compared to the Earth's atmosphere. Ott (1988) interpreted the noble gas data for Chassigny, Shergotty, and EET79001 impact glass to be variable mixtures of two Martian components, an atmospheric one represented by EET79001 glass and an interior component represented by gas in Chassigny.
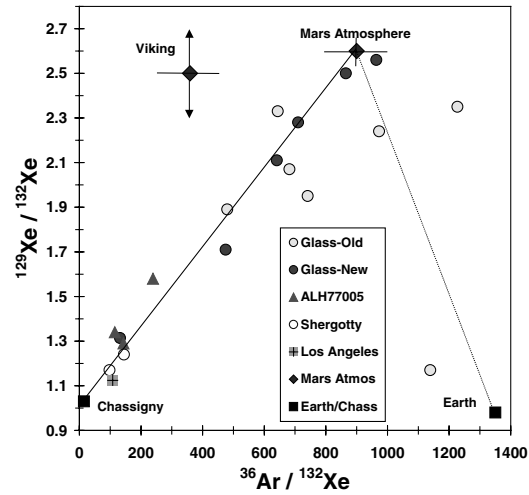
Figure 2. Plot of measured $^{129}Xe/^{132}Xe$ ratios against trapped $^{36}Ar/^{132}Xe$ ratios for various samples of shergottites. The light- and dark-tinted circles represent older and newer analyses, respectively, of impact glass. Other analyses shown are of bulk samples. Chassigny is believed to contain only a Martian interior component, whereas the impact glass contains mostly Martian atmosphere. The atmospheric composition reported by Viking and that indicated by glass data are shown. See text and Table I for relative uncertainties in these data. Two component mixing lines between Mars atmosphere and Mars interior components and between the Martian and terrestrial atmospheres are indicated. Sources of shergottite data are given in Bogard and Garrison (1998) and Garrison and Bogard (2000).
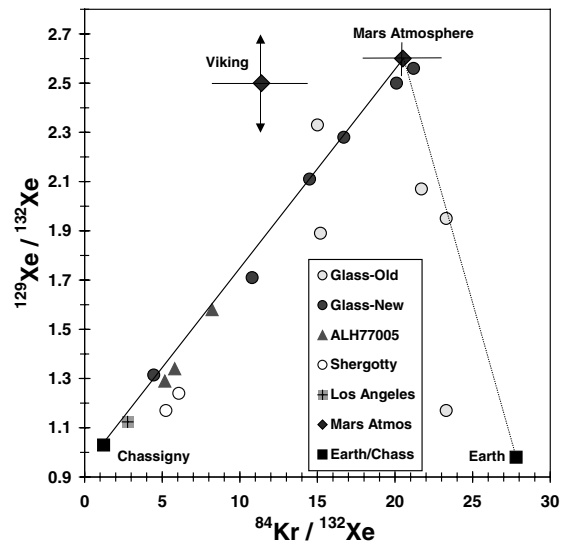

Figure 3. Plot of the measured $^{129}Xe/^{132}Xe$ ratio against the $^{84}Kr/^{132}Xe$ ratios for various samples of shergottites. See Figure 2 caption for sample explanations.

It is now apparent that both Martian atmospheric and interior components of Ar, Kr, Xe, and N, occur in Martian meteorites, with the atmospheric component being dominant in shergottite impact glass (Table I). Figures 2 and 3 illustrate these two-component mixtures for noble gases in several Martian meteorites. The elemental ratios ^{36}Ar/^{132}Xe and ^{84}Kr/^{132}Xe are plotted against the ^{129}Xe/^{132}Xe ratio because the latter is very different for the atmospheric and interior components and can generally be measured with good precision. Some data on a single impact glass inclusion, EET79001,27, and data on two Zagami glass inclusions show significant scatter on these plots. Although not always given, analytical uncertainties for most elemental abundances are of the order of $\pm 10\%$ (or $\sim \pm 15\%$ in elemental ratios), and thus do not explain the entire scatter in the data. Part of the data scatter is likely caused by the presence of a third component, e.g., terrestrial air. (Note that one glass inclusion (EET79001,54) plots close to the terrestrial composition in the lower right of both Figures 2 and 3.) However, recent analyses of melt glass from Shergotty, Y-793605, two different melt inclusions of EET79001, and shocked portions of ALH77005 give linear mixing relations for both the ^{36}Ar/^{132}Xe and ^{84}Kr/^{132}Xe ratios (Figures 2 and 3; Bogard and Garrison, 1998). The mixing trend for these shergottites passes through the composition measured in Chassigny (Ott, 1988), which contains the interior volatile component, but no atmospheric component. These mixing relations define Martian atmospheric ^{36}Ar/^{132}Xe $= 900 \pm 100$ and ^{84}Kr/^{132}Xe $= 20.5 \pm 2.5$, assuming an atmospheric ^{129}Xe/^{132}Xe ratio of 2.6 ± 0.05 (Bogard and Garrison, 1998).

Derivation from meteorite data of accurate Ar/Kr/Xe elemental ratios for the Martian atmosphere requires knowledge of the recent atmospheric ^{129}Xe/^{132}Xe ratio. Unfortunately, some uncertainty exists in this value. The highest ratio reported for an individual temperature extraction of EET79001 impact glass is 2.59 ± 0.03 (Bogard and Garrison, 1998), and is the basis for the atmospheric value of 2.6 assumed in deriving elemental ratios above. Other ^{129}Xe/^{132}Xe measurements in shergottite glass give somewhat lower maximum values of 2.35–2.43 (Swindle *et al.*, 1986; Marti *et al.*, 1995; Mathew *et al.*, 1998). Martian atmospheric Xe present in Nakhla has ^{129}Xe/^{132}Xe of 2.35 ± 0.03 (Gilmour *et al.*, 1999; 2001), and the maximum ratio measured in ALH84001 is 2.16 (Gilmour *et al.*, 1998; Garrison and Bogard, 1998; Mathew and Marti, 2001). It is difficult to envision how ^{129}Xe/^{132}Xe in young impact glass might be increased above the atmospheric ratio, but it might be lowered by mixing of Martian atmosphere with another component. However, if we assume that the atmospheric ^{129}Xe/^{132}Xe ratio is as low as 2.4, the mixing trend in Figures 2 and 3 imply that ^{36}Ar/^{132}Xe $\cong 770$ and ^{84}Kr/^{132}Xe $\cong 18$.

The recent Martian atmospheric composition defined by shergottite glass data in Figures 2 and 3 can be compared with the analyses made by Viking (Table I). Although the two data sources give the same ^{129}Xe/^{132}Xe ratio, the Viking measurement ($2.5, {}^{+2}_{-1}$ has a large uncertainty. *The ^{36}Ar/^{132}Xe and ^{84}Kr/^{132}Xe elemental ratios determined from shergottite data are higher than those measured by Viking by factors of 2.5 and 1.8, respectively, if atmospheric ^{129}Xe/^{132}Xe $= 2.6$, and higher*

by factors of 2.2 and 1.6, respectively, if ^{129}Xe/^{132}Xe = 2.4. The differences in these elemental ratios from Viking and those derived for shergottites fall outside of their combined uncertainties. It seems unlikely that these ratios have changed drastically within the last ∼0.2 Gyr, and the shergottite data probably represent the recent Martian atmospheric composition more accurately. The shergottite impact glass values for ^{36}Ar/^{132}Xe and ^{84}Kr/^{132}Xe are within a factor of ∼1.5 of the terrestrial values and indicate even greater similarity in relative noble gas abundances between the two planetary atmospheres than suggested by Viking data.

Assuming the shergottite glass values of these elemental ratios are correct, this requires adjustment of the mixing ratios of noble gases in the Martian atmosphere. If we adopt the shergottite elemental ratios derived for the case that ^{129}Xe/^{132}Xe = 2.6, adopt the Viking atmospheric mixing ratio for ^{40}Ar of 1.6%, and assume atmospheric ^{40}Ar/^{36}Ar $\cong$ 1800 (see later section), we can calculate revised Martian atmospheric abundances. The Kr abundance becomes 0.36 ppm, or about 20% larger than that reported by Viking, and the Xe abundance becomes 0.05 ppm, or only 65% of that reported by Viking. The ^{36}Ar mixing ratio is ∼9 ppm. Similarly, the trapped ^{20}Ne/^{36}Ar ratio of ∼0.1 in shergottite impact glass reported by Garrison and Bogard (1998) implies that the Ne mixing ratio on Mars is only ∼1 ppm, a value which lies at the lower limit of the value (2.5, $^{+3.5}_{-1.5}$ ppm) reported by Viking. Given the relatively large uncertainties for much of the Viking measurements, these revised mixing ratios do not present a discrepancy.

2.4. FRACTIONATED AND ANCIENT ATMOSPHERIC GASES

The nakhlites and ALH84001 possess Martian atmospheric noble gases that appear to have been fractionated in their elemental ^{36}Ar/Xe and Kr/Xe ratios, compared to those in shergottite impact glass. In addition, at least ALH84001 contains trapped N and Xe that appear isotopically unfractionated and which may represent a trapped ancient Martian atmosphere.

Ar, Kr, and Xe data for the nakhlites and ALH84001 suggest a two component mixing trend, which passes close to the Chassigny point, but which is rotated counter-clockwise compared to the mixing trend defined by shergottite data in Figures 2 and 3 (Ott, 1988; Drake *et al.*, 1994; Swindle *et al.*, 1995; Miura *et al.*, 1995; Murty and Mohapatra, 1997; Gilmour *et al.*, 1998; Bogard and Garrison, 1998; Mathew *et al.*, 1998; Gilmour *et al.*, 2001). Although the data show some scatter, they appear to be consistent with mixing of an interior component similar to that found in Chassigny with a different type of atmosphere-like component. Swindle *et al.* (1995) concluded, based on a lack of a correlation of the ^{129}Xe/^{132}Xe and ^{136}Xe/^{132}Xe ratios, that a two-component mixture of Martian atmospheric Xe and solar-type Xe does not explain bulk ALH84001 data. The maximum ^{129}Xe/^{132}Xe ratio in Nakhla, 2.35 ± 0.03, is comparable to that in the glass of shergottites and could be largely modern, but might be as old as the 1.3 Gyr formation age of Nakhla. (ALH84001 is the only known Martian meteorite older than 1.3 Gyr.) The

highest measured $^{129}Xe/^{132}Xe$ ratio of 2.16 in ALH84001 is outside the range of 2.35–2.59 observed for the recent Martian atmospheric component in shergottites and may represent ancient (i.e., $\sim$4 Gyr; Turner *et al.*, 1997) trapped atmospheric gas. Other isotopic and elemental compositions in ALH84001 are $^{36}Ar/^{38}Ar \geq 5.0$, $^{36}Ar/^{132}Xe \sim 50$, and $\delta^{15}N = 7\%o$ (Mathew and Marti, 2001; Table I).

The elementally fractionated noble gas data of ALH84001 and the nakhlites have been interpreted in two ways. The first interpretation is that the noble gas composition is an outcome of solubility controlled fractionation during direct incorporation of atmospheric gases into Martian weathering products (Drake *et al.*, 1994), as commonly occurs with terrestrial rocks (Ozima and Podosek, 1983). A second interpretation is that the elemental fractionation may have occurred during adsorption of atmospheric gases onto mineral surfaces, followed by shock implantation (Gilmour *et al.*, 2001). In contrast to Nakhla, ALH84001 silicates do not exhibit signs of alteration by liquid water, and elemental fractionation involving aqueous alteration is less likely. Using laser probe analyses of individual mineral grains, Gilmour *et al.*, (1999; 2001) demonstrated that the major carrier of the atmospheric Xe in Nakhla is actually pyroxene, with only a minor proportion being present in weathering products. Gilmour *et al.* (2001) concluded that a Chassigny-like interior component was present in Nakhla and was concentrated in feldspar. These authors argue that differences in gas release between Nakhla and ALH84001 may relate to differences in shock levels, high in ALH84001 and low in Nakhla, and that these are reflected in the corresponding (high and low) release temperatures of the atmospheric components for the two meteorites.

Most workers assume that the shock-implanted atmospheric component in shergottite glass is likely to have been much less elementally fractionated than was the component incorporated into the nakhlites and ALH84001 (e.g., see Bogard *et al.*, 1986; Drake *et al.*, 1994). If we assume that the $^{36}Ar/^{132}Xe$ and $^{84}Kr/^{132}Xe$ ratios derived above for the Martian atmosphere are correct, then the average value for this atmospheric component in the nakhlites and ALH84001 has been fractionated in favor of the heavier species by factors of approximately 15 and 2.6, respectively (Bogard and Garrison, 1998), well outside experimental uncertainties. For a $^{129}Xe/^{132}Xe$ ratio in the Martian atmosphere of <2.6, these fractionation factors would be proportionally less.

2.5. ARGON ISOTOPIC COMPOSITION

Analyses of shergottite impact glass indicate a lower value for the $^{40}Ar/^{36}Ar$ ratio of the Martian atmosphere compared to the Viking value of 3000 ± 500. Determination of this ratio in shergottites is not straightforward because of the presence of additional Ar components, including radiogenic ^{40}Ar from in situ decay of ^{40}K, cosmogenic ^{36}Ar, trapped Martian interior Ar, and sample contamination by terrestrial Ar. For example, using literature data and specific values for formation ages and space exposure ages for several Martian meteorites, Terribilini *et al.* (1998)

corrected total ^{40}Ar for *in situ* decay of ^{40}K and corrected total ^{36}Ar for cosmogenic ^{36}Ar in order to derive trapped ^{40}Ar/^{36}Ar ratios. These ^{40}Ar/^{36}Ar ratios varied widely, from ∼200 to ∼1900, indicating more than one trapped Ar component.

Two lines of evidence indicate that the ^{40}Ar/^{36}Ar ratio for trapped Martian atmosphere in shergottites actually lies in the range 1600–1900. First, a plot of ^{40}Ar/^{36}Ar against ^{129}Xe/^{132}Xe for various shergottite samples shows two component mixing between Martian atmospheric and interior components (Garrison and Bogard, 1998 and references therein). For values of ^{129}Xe/^{132}Xe approaching the maximum measured value of 2.59, the ^{40}Ar/^{36}Ar ratios approach an upper limit of ∼1900. The second line of evidence for a lower atmospheric ^{40}Ar/^{36}Ar than the Viking measurement comes from shergottite samples neutron-irradiated for ^{39}Ar-^{40}Ar dating (Bogard and Garrison, 1999). Higher temperature extractions of shergottites EET79001 and ALH77005 each released ∼61% of the total Ar and, when plotted on a modified isochron plot of ^{36}Ar/^{40}Ar versus ^{39}Ar/^{40}Ar, defined intercepts on the ^{36}Ar/^{40}Ar axis of ^{40}Ar/^{36}Ar = 1735 ± 85 and 1760 ± 100, respectively. Because the abundance of trapped ^{40}Ar greatly dominates over radiogenic ^{40}Ar in these two samples, only a very short extrapolation of the mixing trend from the data to the ^{36}Ar/^{40}Ar axis is required. In addition, most extractions of a sample of Shergotty define a linear trend giving a ^{39}Ar-^{40}Ar age of ∼167 Myr and a ^{40}Ar/^{36}Ar trapped ratio of ∼1780. Lower temperature extractions of shergottites suggest release of terrestrial atmospheric Ar and possibly some Martian interior Ar. For this reason, the largest measured trapped ^{40}Ar/^{36}Ar ratios in these samples are considered to better represent the Martian atmospheric value. Although the atmospheric ^{40}Ar/^{36}Ar ratio may change with time, it is unlikely that this ratio evolved from ∼1800 to the Viking value of ∼3000 over the past 0.2 Gyr. *Thus, we conclude that an atmospheric ^{40}Ar/^{36}Ar ratio of 1800 ± 100 probably represents the present Martian atmosphere.*

Attempts have also been made to measure the ^{40}Ar/^{36}Ar ratio of the Martian interior component. The shergottite analyses by Bogard and Garrison (1999) suggest that this component is released at intermediate extraction temperatures and has a ^{40}Ar/^{36}Ar ratio of <500. For EET79001 glass, Wiens (1988) estimated the interior ^{40}Ar/^{36}Ar at 430–680. The ^{40}Ar/^{36}Ar ratios in the high temperature releases of Chassigny suggest interior ^{40}Ar/^{36}Ar is <206; the lowest ^{40}Ar/^{36}Ar ratio in ALH84001 is 128, observed at the highest release temperature (Mathew and Marti, 2001), and may indicate a much lower value for this atmospheric ratio early in Martian history. However, partitioning of atmospheric and interior Ar components in ALH84001 is not well constrained, and this low ratio may also reflect an interior Ar component. Because ^{40}Ar and ^{36}Ar in the interior have completely different sources (radiogenic and primordial, respectively), the two isotopes evolved separately over time and probably are heterogeneously distributed within Mars. Thus the interior ^{40}Ar/^{36}Ar ratio probably is not the same everywhere.

In addition to an ∼62% enrichment in the ^{15}N/^{14}N ratio, the isotopic compositions of Ar, Xe and H also show significant isotopic fractionation due to atmo-
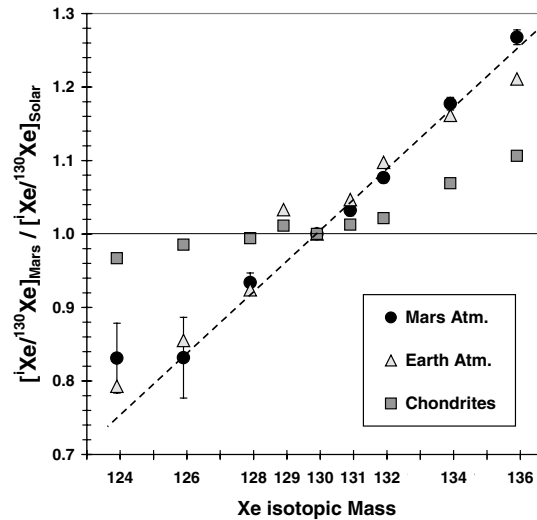
Figure 4. Isotopic composition of Xe in EET79001 impact glass (Swindle *et al.*, 1986), normalized to the solar Xe composition and mass 130. Also shown are the normalized Xe compositions for the Earth and primitive chondrites (Pepin, 1991). The dashed line indicates a possible mass fractionation trend for Martian Xe relative to solar Xe.

spheric loss. Even in the earliest analyses of impact glass in EET79001, several investigations noted *the presence of trapped Ar with a $^{36}Ar/^{38}Ar$ ratio considerably less than the terrestrial value of 5.32.* Wiens *et al.* (1986) deduced a Martian atmospheric ratio of 4.1. Swindle *et al.* (1986) derived a value of 3.60 ± 0.44. Bogard (1997) considered all shergottite data available up to that time and concluded that the ratio is less than 3.9. Deriving a precise value for Martian atmospheric $^{36}Ar/^{38}Ar$ is made difficult because of the presence of significant amounts of Ar produced by cosmic ray reactions during space exposure of Martian meteorites. The most accurate determinations derive from the EET79001 impact glass. (EET79001 has a relatively low exposure age of $\sim$0.6 Myr.) Such a low $^{36}Ar/^{38}Ar$ as that indicated for the Martian atmosphere is unique in the solar system (except for minor components produced by cosmic ray interactions). In contrast, Chassigny contains a trapped Martian interior component for which the $^{36}Ar/^{38}Ar$ ratio is $\geq$5.26 (Mathew and Marti, 2001). For comparison, this ratio is 5.32 in the Earth's atmosphere and $\sim$5.7 in the solar wind (Pepin *et al.*, 1995).

2.6. XENON ISOTOPIC COMPOSITION

The Viking Xe analyses had large uncertainties, and only the $^{129}Xe/^{132}Xe$ ratio was reported. Trapped Martian atmosphere in shergottite glass yields much more accurate isotopic data. The Xe composition of EET79001 impact glass (Swindle *et al.*, 1986) precisely agrees with shergottite glass data given by Mathew *et al.*

(1998). An informative way to consider this Xe composition is to compare it to Xe in other major volatile reservoirs and to assess the possibility that the Martian atmospheric composition was derived from one of these other reservoirs. Figure 4 plots the EET79001 Xe isotopic composition normalized to the solar wind composition (Pepin *et al.*, 1995) and to ^{130}Xe. In Figure 4 the solar composition is represented by the horizontal line and the difference between the Martian atmosphere and solar composition for a given ^{i}Xe/^{130}Xe isotopic ratio is proportional to the separation from the horizontal line. The isotopic compositions of Xe in the Earth's atmosphere and in primitive chondritic meteorites (Pepin, 1991) are also plotted relative to solar Xe. It is obvious that *the isotopic composition of Martian atmospheric Xe, as represented by EET79001 impact glass, closely resembles the terrestrial composition*, the only appreciable difference being for ^{136}Xe, which includes a fission component. (In discussing the Xe isotopic composition here we ignore ^{129}Xe, which contains a major component from decay of extinct ^{129}I.) Martian atmospheric Xe clearly differs from the solar and chondritic Xe compositions.

A characteristic of this type of isotope plot is that, for small mass intervals, derivation of one Xe component from a second Xe component by mass fractionation will cause the second composition to rotate about the first while maintaining an approximately linear relationship. Swindle *et al.* (1986) normalized their Martian Xe composition to chondritic Xe. Except for masses 126 and 128, Xe in EET79001 glass was generally consistent with derivation from chondritic Xe by mass fractionation, where the Martian ^{136}Xe/^{130}Xe ratio was enriched by ~15%. However, Martian atmospheric Xe also closely resembles mass fractionated solar Xe (Swindle and Jones, 1997; Mathew *et al.*, 1998), as indicated by the dashed line in Figure 4. Using an initial solar composition, Mathew *et al.* (1998) derived a linear mass fractionation of 37‰ (3.7%) per amu, or twice as much as required for an initial chondritic composition. It is obvious that if the starting Xe composition for the Martian atmosphere resembled either solar or chondritic Xe, it has been strongly mass fractionated in favor of heavier isotopes.

In addition to the presence in the Martian atmosphere of excess ^{129}Xe from ^{129}I decay, one might also expect $^{131-136}$Xe from the fission of ^{235,238}U and extinct ^{244}Pu ($t_{1/2} = 82$ Myr). Fission Xe apparently is present in the Earth's atmosphere (Ozima and Podosek, 1983; Porcelli and Wasserburg, 1995). Swindle and Jones (1997) argue that a chondritic initial Xe composition also implies an unreasonable fractionation of I from Pu+U in the interior of Mars in order to generate significant quantities of excess radiogenic ^{129}Xe in the Martian atmosphere, but little fission Xe. These authors suggest that the starting composition for the fractionated Martian atmosphere was solar Xe, which permits a somewhat higher concentration level of fission Xe in the current atmosphere. In addition, Mathew *et al.* (1998) present stepwise temperature data for Xe in shergottites that are consistent with mass fractionated solar Xe plus small additions of fission Xe. In further support of a solar Xe starting composition is the observation of Xe with a solar composition trapped in the Chassigny meteorite and solar Kr in the present atmosphere (see
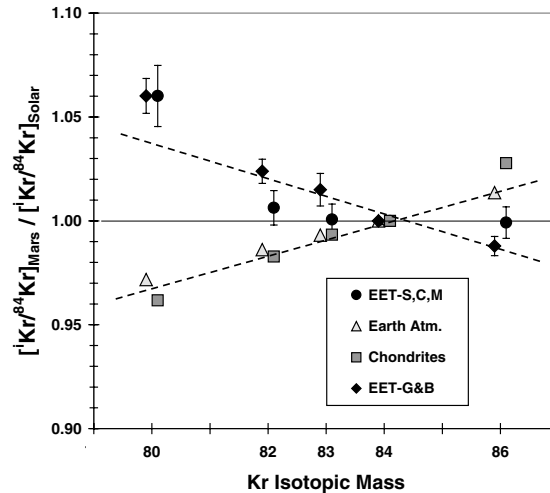
Figure 5. Isotopic composition of Kr in two samples of EET79001 impact glass (S,C,M=Swindle *et al.*, 1986; G&B=Garrison and Bogard, 1998, plotted normalized to the solar Kr composition K-1 (Pepin *et al.*, 1995) and mass 84. Also shown are the Kr compositions for the Earth and primitive chondrites (Pepin, 1991), also normalized to solar Kr and mass 84. The two dashed lines show mass fractionation trends (relative to solar K-1) for chondritic Kr and the maximum mass fractionation for Martian atmospheric Kr.

discussion below). If the dashed mass fractionation line of Martian Xe relative to solar Xe in Figure 4 had a somewhat lesser slope, it would agree better with the light Xe isotopic data of EET79001 and would permit small excesses of fission Xe at masses 132–136. In this case the $^{136}Xe/^{130}Xe$ mass fractionation relative to solar would be ~20%. It is not yet possible to model completely unambiguously those specific processes and starting compositions that have created the present Martian atmosphere, although a solar-like starting composition seems likely.

2.7. KRYPTON ISOTOPIC COMPOSITION

The isotopic composition of Kr in the Martian atmosphere, as measured in shergottite impact glass, presents some intriguing contrasts with the evidence for strong mass fractionation of Ar and Xe. Figure 5 plots the isotopic composition of Kr measured in two glass inclusions of EET79001, normalized to mass 84 and to the K-1 solar Kr composition derived by Pepin *et al.* (1995) from analyses of solar gases in lunar fines. The normalized compositions of Kr in the terrestrial atmosphere and in primitive chondritic meteorites are also shown (Pepin, 1991). The plotted data of Swindle *et al.* (1986) were summed over seven temperature extractions of impact glass EET79001,27. The plotted data of Garrison and Bogard (1998) are the 1550°C extraction of impact glass EET79001,8A, which released 78% of the total Kr in this sample. Garrison and Bogard (1998) suggested that the Kr released

at lower extraction temperatures from both samples contained terrestrial Kr contamination, which would cause rotation of the measured shergottite composition counter-clockwise toward the terrestrial data (compare Figure 5). An average Kr composition derived from three high temperature extractions from Swindle *et al.* (1986) and three high temperature extractions from two different EET79001 glass inclusions from Garrison and Bogard (1998) is similar to the 1550°C composition of EET79001,8A plotted in Figure 5.

From Figure 5 it is obvious that both the chondritic and terrestrial Kr compositions appear mass fractionated in favor of heavier isotopes relative to solar Kr, except for a small excess in chondritic ^{86}Kr (which may be affected by fission products). Swindle *et al.* (1986) originally normalized both their Kr and Xe data for EET79001 impact glass to the chondritic composition. A chondritic normalization would imply that Martian atmospheric Kr is mass fractionated in favor of lighter isotopes by almost 1%/amu. This is opposite to the apparent enrichment of heavier isotopes of Xe when normalized to a chondritic composition and to the observed enrichment of ^{38}Ar over ^{36}Ar. Clearly such opposite mass fractionation for Kr cannot be produced by the process that produced Xe and Ar fractionation. This, along with the evidence for solar Xe inside Mars (discussed below), suggests that the Martian Kr composition is more appropriately compared to solar Kr, as is done in Figure 5.

Analyses of Kr in EET79001 impact glass indicate that a small excess exists at mass 80 (and possibly mass 82) relative to the fractionation trend defined by either a chondritic or solar normalization (Becker and Pepin, 1984; Swindle *et al.*, 1986; Garrison and Bogard, 1998). This excess ^{80}Kr is probably caused by neutron-capture by ^{79}Br at the Martian surface, where the neutrons are produced from cosmic ray interactions.

Pepin (1991) noted that the Kr composition reported by Swindle *et al.* (1986) and the K-1 solar composition are essentially identical (when a neutron-capture component has been removed) and concluded that Martian atmospheric Kr is unfractionated solar Kr. On the other hand, if the Kr composition given by Bogard and Garrison (1998) is used to represent the Martian atmosphere, then Martian atmospheric Kr appears to be mass fractionated relative to K-1 solar Kr by ~0.5% per mass unit in favor of lighter isotopes. A possible explanation of this fractionation is that the composition of solar Kr is not precisely defined. Different lunar and meteorite samples containing solar Kr show variations of as much as ~2% at individual masses (Pepin *et al.*, 1995), and Pepin (1991) considered a possible uncertainty in the solar Kr composition of ~0.5%/mass. We tend to reject the occurrence of isotopic fractionation during gas implantation into the impact melt, because laboratory experiments do not suggest isotopic fractionation during shock implantation (Bogard *et al.*, 1986). It is possible, however, that solar wind Kr implanted into lunar and meteorite samples has been slightly mass fractionated relative to solar Kr initially acquired by Mars. Thus, we conclude that *within present uncertainties, the isotopic compositions of Martian atmospheric Kr and solar Kr do not differ.*

2.8. NEON ISOTOPIC COMPOSITION

Viking reported only 2.5 ($^{+3.5}_{-1.5}$) ppm Ne in the Martian atmosphere and was unable to measure its isotopic composition (Owen *et al.*, 1977). (We noted above that the shergottite glass data suggest only $\sim$1 ppm Ne.) Given the large mass fractionation observed in D/H, $^{15}N/^{14}N$, and $^{36}Ar/^{38}Ar$, one would expect the $^{20}Ne/^{22}Ne$ ratio also to be strongly mass fractionated. Neon compositions measured in impact glass of shergottites are ambiguous on this point, however. Garrison and Bogard (1998) plotted $^{20}Ne/^{22}Ne$ ratios against $^{21}Ne/^{22}Ne$ ratios for stepwise temperature extractions of impact glasses from three shergottites as measured in three different laboratories. In general, the data indicate a two-component mixture between cosmogenic Ne and a trapped component, but the data show significant scatter. Scatter in the cosmogenic composition exists because of the possible presence of Ne produced by energetic solar protons and because different Na/Mg concentration ratios in some samples produced different cosmogenic $^{21}Ne/^{22}Ne$ ratios. It is not clear why apparent variations exist in the $^{20}Ne/^{22}Ne$ ratio of the trapped component. Most data suggest a trapped ratio somewhat similar to the terrestrial ratio of 9.8, but some data are consistent with lower values. The trapped component tends to be released at lower extraction temperatures, and part of this release may consist of terrestrial Ne contamination in the samples. The degree of mass fractionation of $^{20}Ne/^{22}Ne$ in the Martian atmosphere, if any, is thus poorly constrained. If solar Ne with $^{20}Ne/^{22}Ne \geq 13$ were the starting composition, significant fractionation is suggested. However, if chondritic-like Ne with $^{20}Ne/^{22}Ne \cong 8.2$ were the starting composition, no significant fractionation is indicated.

3. Interior Nitrogen and Noble Gas Components

As pointed out above, the Chassigny meteorite contains primarily a Martian interior component that is very different in composition from the Martian atmospheric component. Derivation of the composition of this interior component is more difficult compared to the atmospheric component, and the interior composition reported in Table I has been deduced from several meteorite sources. In comparisons of relative abundances of trapped Ar, Kr, and Xe and the $^{129}Xe/^{132}Xe$ and $^{15}N/^{14}N$ isotopic ratios, the shergottites apparently contain variable mixtures of the Martian atmospheric component and the Martian interior component, (Figures 2 and 3). Some samples also contain varying amounts of terrestrial noble gas contamination. Noble gases from shergottites EET79001, Shergotty, Zagami, ALH77005, Yamato-793605, LEW-88516, DaG-476, Los Angeles, Dhofar-019, and Sayh al Uhaymir-005 are consistent with variable mixtures of these three gas components (Zipfel *et al.*, 2000; Shukolyukow *et al.*, 2000; Garrison and Bogard, 2000; Mohapatra and Ott, 2000; earlier data references in Bogard and Garrison, 1998). Analyses of some of these shergottites indicate the presence of the Martian interior component, but little of the Martian atmospheric component.

Recent investigations of Xe isotopes released at different temperatures show substantial variations and indicate that the Martian interior gas component actually consists of two or more components (Mathew and Marti, 2001). The Chass-S (Solar) gases in Chassigny (Mathew and Marti, 2001) represent an elementally heavily fractionated reservoir. These authors noted that a second composition, Chass-E (Evolved), can be related to Chass-S by addition of ^{244}Pu fission Xe component. However, the Chass-E xenon defines a uniform trapped signature and implies that the fission Xe component was well mixed with the solar Xe component at the time of incorporation and that in-situ decay of ^{244}Pu can be ruled out. Therefore, both Chass-S and Chass-E represent interior reservoirs of Mars and both are characterized by low $^{129}Xe/^{132}Xe$ ratios (<1.07). The $^{36}Ar/^{132}Xe$ and $^{84}Kr/^{132}Xe$ ratios associated with Chass-S and Chass-E are constrained to be, <5 and <1.1, and >130 and >1.8, respectively. The amount of ^{244}Pu-Xe that needs to be added to Chass-S to generate Chass-E is 8.4% of the total ^{136}Xe in Chassigny. The implied $^{244}Pu/^{238}U$ ratio at the time of system closure is 0.002. It is not clear why Chassigny contains Xe with a solar-like composition while showing such strong fractionation in Ar/Kr/Xe elemental abundances.

The bulk Chassigny data of Mathew and Marti (2001) show light N isotopic signatures in the ≤300°C extractions ($\delta^{15}N \leq -21‰$). The heaviest signature these authors observed in the low-temperature range is $\delta^{15}N = +15‰$ at 400°C. Interestingly, the N signatures observed in the intermediate temperature steps of ALH84001 and Chassigny are rather similar. Further, the light N is enriched in Chassigny olivine inclusions, and the signature of the light nitrogen ($\delta^{15}N = -30‰$) observed in the olivine is consistent with light N measured in ALH84001. This light nitrogen signature apparently represents the primitive interior nitrogen reservoir, which did not exchange with the evolving atmospheric nitrogen.

4. Isotopes of O, C, H, and S

On Earth, all waters and almost all rocks have oxygen isotopic compositions that lie on a single fractionation line in a three-isotope graph of $\delta^{17}O$ versus $\delta^{18}O$. (Here the δ notation indicates deviation in the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios in parts per thousand relative to standard mean ocean water, SMOW.) The known exceptions are some sulfate rocks with a ^{17}O-excess ultimately derived from atmospheric ozone, which has a large isotopic anomaly (Thiemens *et al.*, 1995). The observation derived from Martian meteorites that carbonates and hydroxyl minerals have oxygen isotopic compositions displaced from the principal fractionation line defined by silicates implies the existence on Mars of volatile reservoirs (e.g., atmosphere and hydrosphere) that are not isotopically buffered by the major rock reservoir. Thus, the terrestrial model of recycling of water and carbon dioxide through the rocky interior is not applicable to Mars. The isotopic composition of oxygen (and probably hydrogen and carbon) must be dominated by sources and/or processes outside the

rock reservoir. These include: (1) continued or late addition of cometary volatiles to the atmosphere (Owen and Bar-Nun, 1995a), (2) anomalous isotopic fractionation during escape of gases from the atmosphere (Jakosky, 1993), or (3) photochemical processes analogous to those occurring today in the terrestrial stratosphere (Thiemens *et al.*, 1995).

Most carbonates in SNC meteorites have $\delta^{18}O$ values of $+20$ to $+40‰$, which are much higher than the average $\delta^{18}O$ of $+4$ to $+5‰$ for the silicate minerals. Clayton and Mayeda (1984) attempted to account for this large difference by postulating high-temperature planetary outgassing of both CO_2 and H_2O, followed by low-temperature re-equilibration of the volatiles with one another, leading to ^{18}O-enrichment in the CO_2. This mechanism is inconsistent with the more recent observations that oxygen in carbonates and hydroxyl minerals does not lie on the rock fractionation line (Karlsson *et al.*, 1992; Farquhar *et al.*, 1998).

The oxygen isotopic compositions of carbonates in ALH 84001 are quite remarkable, ranging from $-5‰$ to $+30‰$ over distances of <1 mm (Leshin *et al.*, 1998; Saxton *et al.*, 1998; Holland *et al.*, 2000). Various scenarios have been proposed to account for the isotopic zoning, including temperature variations and precipitation in closed or open systems. Ion microprobe measurements, with good spatial resolution, show that the first-formed carbonates have low $\delta^{18}O$, and later-formed carbonates have progressively higher $\delta^{18}O$. This behavior suggests precipitation in a closed system from a CO_2-rich fluid, in a Rayleigh process (Romanek *et al.*, 1994; Leshin *et al.*, 1998). As noted by Leshin *et al.* (1998), the progressive increase in $\delta^{13}C$ of the carbonates in ALH 84001 requires temperatures above 200°C. On the basis of the preservation of large gradients in chemical and isotopic compositions, Valley *et al.* (1997) estimate an upper limit of about 300°C for carbonate formation (see also Kent *et al.*, 2001).

Carbon isotopes may provide some clues as to the Martian behavior of this important element. The visible inventory of carbon on Mars is only 10^{-3} of that on Earth or Venus. No evidence has been found by instrumented spacecraft for carbonate rocks at the surface. The $^{13}C/^{12}C$ ratio measured by Viking in atmospheric CO_2 resembled the typical terrestrial value, but the measurement uncertainties were very large (Owen *et al.*, 1977). The $^{13}C/^{12}C$ ratio measured in Martian meteorites gives a relatively wide range of $\sim 7.5\%$, but the reasons for these variations are not well understood.

Hydrogen isotopes also show a large difference in abundances between an internal reservoir and the atmosphere/hydrosphere. Minerals from SNC meteorites appear to contain a mixture of a mantle-derived component with $\delta D \sim +900‰$ (Watson *et al.*, 1994; Leshin, 2000 and an atmosphere-derived component with $\delta D \sim +4500$, as measured directly in the Martian atmosphere (Owen *et al.*, 1988; Krasnopolsky *et al.*, 1997). The large deuterium enrichment in the atmosphere is attributed to isotopic fractionation due to Jeans escape of hydrogen (Owen *et al.*, 1988; Yung *et al.*, 1988; Jakosky and Jones, 1997). The two-fold enrichment of D/H in the interior, relative to the terrestrial mean, may also be due to an early loss

of hydrogen, or may result from accretion of deuterium-rich material, as is found in comets (Owen, 1997; Owen and Bar-Nun, 2000; Leshin, 2000) and in organic matter of carbonaceous chondrites (Robert and Epstein, 1982). In both cases, the deuterium enrichment probably resulted from low-temperature ion-molecule reactions in the interstellar cloud preceding formation of the solar system (Geiss and Reeves, 1981; Meier and Owen, 1999).

Sulfur plays several important roles in the geochemistry of Mars. As a moderately volatile element, it is probably depleted in the bulk chemical composition of the planet relative to chondritic or solar abundances. As in the case of potassium (Humayun and Clayton, 1995), planetary accretion processes seem to have brought about elemental depletions of sulfur by perhaps a factor of 5–10, without concomitant stable isotope fractionation. The planetary abundance of sulfur in Mars is unknown, and a major fraction of it may be in the core (Schubert and Spohn, 1990). On the Martian surface, chlorine and sulfur are much more abundant in soils and dust than in the underlying rocks (Rieder *et al.*, 1997), implying an origin by volcanism, some chemical transformation in the atmosphere, and eolian or aqueous deposition. Sulfur isotope measurements on returned Martian samples should have high priority.

On Earth, sulfur isotope fractionation in igneous processes produces a range of δ^{34}S of a few permil (Ohmoto, 1986), with the average of mantle-derived samples being indistinguishable from the Canyon Diablo meteorite standard. Much larger variations are found in crustal rocks, which have experienced low-temperature processing and oxidation-reduction chemistry. These low-temperature processes are commonly facilitated by biological systems; hence, large sulfur isotope variations are sometimes used to implicate biological processes in geological environments. A simple counter-example shows that this is not an infallible tool: sulfur isotopes are strongly fractionated in lunar soils due to micrometeorite bombardment and consequent vapor loss (Clayton *et al.*, 1974, and references therein). Sulfur isotope studies of SNC meteorites have had two goals: (1) a search for evidence of biological processes, and (2) a search for evidence of atmospheric chemical processes. Shearer *et al.* (1996) and Greenwood *et al.* (1997) used ion microprobe techniques to study sulfides in ALH 84001 and found a modest range of δ^{34}S, from +2.0 to +7.3‰. The range found for shergottites was -1.9 to +2.7‰. These values are all compatible with origins in igneous and hydrothermal processes, and show no large effects such as are seen on Earth in bacterial processes.

On Earth, atmospheric oxidation of volcanic sulfur-bearing gases may lead to non-mass-dependent isotopic fractionation, which manifests itself as excesses or deficiencies of ^{17}O and/or ^{33}S in the sulfate products (Bao *et al.*, 2000; Farquhar *et al.*, 2000a). Farquhar *et al.* (2000b) analyzed sulfides and sulfates from three shergottites and two nakhlites, and found small ^{33}S deficits in two samples of Nakhla, whereas all other samples showed no non-mass-dependent effects. The mass-dependent variations in δ^{34}S ranged from -5 to +5‰ with both ends of this range representing sulfates. Thus the isotopic signature of Martian atmospheric

chemistry in SNC meteorites is very subtle. A measurement of a returned soil or dust sample should be much more informative.

5. Models for Atmospheric Evolution and Mass Fractionation

A common assumption made about the Martian and terrestrial atmospheres is that the volatiles initially derived from some major reservoir, such as the solar nebula or gases modified during early planetary formation and now present in primitive meteorites and comets. The early planetary atmosphere was then modified by fractionation loss processes and addition of specific components, such as those produced by radioactive decay. In detail, however, the specific sources of these volatiles and the processes that have modified them are not well known. As discussed earlier, we see evidence of appreciable mass fractionation of several volatile species in the Martian atmosphere, with accompanying enrichment of the heavier isotopes. Other elements (e.g., C, O, and S) are apparently buffered by surface reservoirs, and isotopic enrichment is unlikely to exceed several percent. For Kr and Xe, which should not be buffered by a surface reservoir, Kr appears not to be mass fractionated, whereas Xe is strongly fractionated. This observation is an important constraint on models of how isotopic mass fractionation of atmospheric species occurred. In this section we briefly discuss some models that have been presented to explain isotopic fractionation of the Martian atmosphere. Time evolution of the Martian atmosphere through degassing of radiogenic components is discussed in a later section.

5.1. LOSS OF NITROGEN AND NOBLE GASES

Escape from a planetary gravity field often depends on the mass of an atmospheric species. Lighter species have greater velocities and higher scale heights, which gives them larger relative concentrations in the upper atmosphere compared to heavier species. Giant impacts late in the formation of Mars have been postulated to remove part of the early atmosphere (Melosh and Vickery, 1989; Benz and Cameron, 1990; Ahrens, 1990; Pepin, 1997), but such a process alone would not likely produce significant mass fractionation. Noble gases in the atmospheres of the terrestrial planets might have been mass fractionated during thermal escape from smaller planetesimals, which later accreted to form these planets (Donahue, 1986). Hunten *et al.* (1987) presented a model involving hydrodynamic escape of a massive hydrogen atmosphere very early in the history of the terrestrial planets. In this model, the mass outflow of hydrogen from the planetary atmosphere was sufficiently large that it entrained heavier species and isotopically fractionated them in the loss process. On early Mars a hydrogen atmosphere may have been produced by dissociation of abundant water through intense bombardment by energetic radiation from the early sun.

Because of its relatively large atomic mass, Xe is the species least easily lost from the Martian atmosphere. Pepin (1991) proposed that the hydrodynamic escape of an early hydrogen atmosphere on Mars caused loss of almost the entire initial inventory of atmospheric species. Part of the Xe remained and was strongly mass fractionated. Pepin (1991) proposed that most of the present atmospheric inventory for species lighter than Xe was added by planetary degassing during the latter stages of this process, and that a lesser degree of hydrodynamic fractionation of these volatiles could produce the isotopic fractionations observed in Ne and Ar. Later, Pepin (1994) described a more complex atmospheric evolution model that considered loss by hydrodynamic escape, ion sputtering, photochemical dissociation, impact erosion, and carbonate formation. Because addition of Xe with other gases could mask the isotopically fractionated Xe in the atmosphere, the model suggested that a large fraction of the Xe in the interior of Mars was retained in the core and not degassed with other species. However, no experimental evidence for Xe solubility suggests that this is likely.

To explain the similar, non-chondritic ratios of ^{36}Ar/^{84}Kr/^{132}Xe, but very different total pressures observed in the atmospheres of Mars and Earth today requires a non-fractionating process to deplete the Martian atmosphere. Owen and Bar-Nun (1995a; 1995b; 2000) suggested that the heavy noble gases were delivered by icy planetesimals similar to the comets observed today. This model is supported by laboratory studies of the composition of noble gases trapped in amorphous ice forming at temperatures near 50 K, a reasonable value for the formation temperature of comets in the solar nebula between Uranus and Neptune. Owen and Bar-Nun pointed out that a simple mixing line drawn through the (^{36}Ar/^{132}Xe, ^{84}Kr/^{132}Xe) points for the SNC data passes through the Earth's atmosphere point and the 50 K icy planetesimal point. This model gives a value of $\sim$75 mb for the post-bombardment atmospheric pressure on Mars, with a total volatile inventory of at least 7.5 bars of CO_2 and a 750 m deep layer of water over the planet. The model explains the striking similarity in isotopic composition of Martian and terrestrial xenon by postulating that the xenon trapped in comets exhibits the same fractionation from solar xenon that we find in the two atmospheres. However, there is no model yet for how this fractionation occurred (Notesco *et al.*, 1999). Furthermore, we have no measurements of noble gases in comets, although that should change in the next decade as a result of the CONTOUR and Rosetta missions.

In order to explain the Viking discovery that the ^{15}N/^{14}N ratio in the Martian atmosphere is enriched by $\sim$62%, McElroy *et al.* (1976) and McElroy *et al.* (1977) proposed that solar-induced photochemical reactions produce energetic electrons that dissociate the nitrogen molecule. This results in loss of atomic nitrogen over time, with a planetary enrichment of the heavier isotope. The authors proposed that approximately 99% of the original atmospheric N_2 inventory on Mars may have been lost. Nitrogen escape from Mars has been reconsidered by a number of authors, most recently by Fox (1997) and Fox and Hac (1997). Considering all possible pathways, Fox and Hac (1997) conclude that without an early, dense CO_2

atmosphere on Mars, the enrichment of ^{15}N would be even larger than the value of 1.6 observed today. This model is specific for nitrogen and gives initial surface pressures of $\sim$114–500 mb and N_2 column abundances 4–6 times the present value (Fox and Hac, 1997). Uncertainties in the reaction rates for the production of odd nitrogen species in the Martian atmosphere remain a major factor in limiting the precision of these calculations, in addition to uncertainties in the amount of nitrogen being added to the atmosphere through volcanic outgassing and cometary bombardment. The present ^{15}N/^{14}N value on Mars may therefore be accepted as an additional indicator of a dense, early atmosphere, even though the required increase in nitrogen by itself would not produce such an atmosphere. Unfortunately, the models considered to date have treated N_2 and CO_2 as independent gases whose initial abundances can be varied at will. It seems more appropriate to use a ratio in the range of $CO_2/N_2 = 20 \pm 10$, encompassing the values in the atmosphere of Venus and the Earth's volatile reservoir (Owen and Bar-Nun, 1995a).

Jakosky *et al.* (1994) considered the role of atmospheric sputtering after the early period of heavy bombardment in removing Ar and Ne and the combined role of sputtering and photochemical mechanisms in the removal of N_2. Sputtering is defined as ionization of species in the upper atmosphere, their acceleration by local magnetic fields, and subsequent collisions with other atmospheric species, resulting in sufficient momentum transfer that atoms and molecules escape the planet. Because this loss model alone does not explain the current abundances, the authors also invoked selective planetary degassing. Whether or not the isotopic compositions of Ar and Ne changed with time over the past $\sim$3.8 Gyr depends to some extent on any assumed changes in CO_2 pressure. In a more detailed application of the basic model to Ar, Hutchins and Jakosky (1996) estimated that 85–95% of the ^{36}Ar and 70–88% of the ^{40}Ar has been lost from the atmosphere. Nitrogen loss in the basic model was $\sim$99%, but adding more complexity to the model implies even greater amounts of N_2 loss and an initial pressure of 60 mbar or higher. Jakosky *et al.* (1994) conclude that a very early period of hydrodynamic escape of hydrogen is not required to produce the fractionated N, Ar, and Ne composition in the present Martian atmosphere, although this hydrodynamic mechanism is apparently still required to explain Xe fractionation. Kr and Xe are too heavy to escape through the sputtering mechanism.

5.2. SPACECRAFT OBSERVATIONS

Spacecraft studies at Mars indicate that sputtering by itself was probably not responsible for the loss of an early dense atmosphere. Measurements by the ASPERA experiment on the PHOBOS mission suggest an O^+ outflow of about 2×10^{25} ions/s (1.4×10^7 ions cm^{-2} s^{-1}), leading to a total ion escape rate of the order of 1 kg/s (Lundin *et al.*, 1989, 1990; Zakharov, 1992). This rate would lead to the loss of the present atmosphere in about 10^9 years. Lammer and Bauer (1991) and Fox (1993) have shown that the O escape flux generated by dissociative recombination is 3–

6×10^6 cm^{-2} s^{-1}. Luhmann *et al.* (1992) considered the loss of gases by sputtering caused by re-entering O$^+$ ions. Estimates of O escape from this process range from 4×10^5 cm^{-2} s^{-1} (Zhang *et al.*, 1993) to 3×10^6 cm^{-2} s^{-1} (Kass and Yung, 1995). Luhmann (1997) has argued that loss of oxygen caused by oxygen pick-up ions will dominate the loss from dissociative recombination over reasonable changes in the solar EUV flux.

Fox (1997) has modeled the escape fluxes of 11 ions on Mars, establishing the limits imposed by ionospheric production. She found that O$_2^+$ dominated O$^+$ and that "if ions are being swept away at or near their maximum rates, the loss rates inferred are of the same order as or larger than many other non- thermal mechanisms and should be accounted for in models of the history of Martian volatiles". The *upper limit* to the total escape flux from these calculations is 4.4–14.2×10^{25} s^{-1}, about 4 times higher than the value measured by ASPERA. Yet Fox's upper limit is about an order of magnitude *smaller* than the loss rate calculated by Luhmann *et al.* (1992; 1997) that would produce a serious loss of CO$_2$ (0.14 bar) and water ($\sim$50 m) from early Mars if there were enhanced solar EUV.

Although Mars Global Surveyor (MGS) does not directly measure outflowing ions, it does detect a signature of ions being formed in the Martian exosphere. These ions are picked up by the solar wind and are subsequently lost from the Martian inventory. The Electron Reflectometer onboard MGS observed an attenuation in electron flux at the magnetic pileup boundary of Mars (Acuña *et al.*, 1998), which can be reproduced by a model of solar wind electrons impact-ionizing Martian exospheric H and O (Crider *et al.*, 2000). The O loss rate due to electron impact ionization ranges from 2–20×10^{24} s^{-1}, depending on the assumptions made about the solar wind flow geometry and exospheric density. This estimate is comparable to that of Fox (1997) and slightly less than the Phobos ASPERA measurements Lundin *et al.* (1989; 1990).

Likewise, any neutral particles existing above $\sim$300 km altitude are subject to electron impact ionization and subsequent loss. H and O, being the dominant species at high altitude, suffer the greatest loss. Isotopic fractionation occurs naturally by this process because for any species, the loss rates are proportional to the exospheric density. As the atmospheric scale height is mass dependent, electron impact ionization will have an effectively higher rate for lower mass isotopes with larger scale heights.

We conclude from this brief review that the measured values of ion escape are well within theoretical upper limits which themselves are well below the levels required for removal of an early, dense atmosphere. Future results on the escape of ions and neutrals will be produced by the NOZOMI mission, scheduled to arrive at Mars in 2004.

5.3. H, C, and O Fractionation

If we assume that the large observed D/H enrichment in the Martian atmosphere (Table I) occurred by photodissociation of water during the last ~3.5 Gyr, this implies that at least 90% of the original water inventory near the surface of Mars has been lost. On the other hand, the amount of H_2O lost from Mars by this process has been calculated to be only a few meters averaged over the planet's surface (Yung *et al.*, 1988; Kass and Yung, 1995). This is far less than the reservoir of water expected on Mars from the geological evidence of erosion (Carr, 1986) or volcanism (Greeley, 1987), which is tens to hundreds of meters. The resolution of this apparent paradox may lie in a decoupled cometary source for the near-surface water (Owen, 1997; Owen and Bar-Nun, 1998; 2000), which may have had a starting δD of ~900‰ (Watson *et al.*, 1994; Leshin, 2000). This value is similar to the cometary D/H value for H_2O (Meier and Owen, 1999). The small size deduced for the amount of water fractionated by atmospheric escape would in turn derive from the fact that the water involved in this process was only the water left near the surface after ~3.5 Gyr ago, which could be a much smaller amount than the total original inventory. Another possibility is that part of the D/H fractionation occurred during the early hydrodynamic escape of hydrogen (Carr, 1996; Leshin, 2000), if this process indeed took place. In either case, the time at which the main reservoir of water was either segregated or lost is obviously of critical importance. The key constraints on this time may come from dating the erosional features in the Martian landscape.

As noted above, mass fractionation of carbon and oxygen isotopes during loss from the upper Martian atmosphere is mitigated by buffering and exchange with surface reservoirs of CO_2. To explain an observed range in $^{13}C/^{12}C$ in Martian meteorites of ~7.5%, Jakosky (1991) estimates that 40–70% of the carbon exchanging with the atmosphere has been lost to space, but this value would be higher if significant late planetary degassing occurred over time. The $^{18}O/^{16}O$ ratios in Martian meteorite carbonates imply a ratio in the atmosphere that is enriched by ~3.5% in ^{18}O. With this assumption, Jakosky (1991) estimates that 20–30% of the oxygen in the surface-atmosphere exchangeable system (primarily H_2O and CO_2) has been lost to space. If we take the existing Martian polar caps and regolith to be the only exchangeable surface reservoir, this implies that the amounts of CO_2 and water lost to space cannot have exceeded 0.25 bar and 5 m, respectively (Jakosky and Jones, 1997). This assumes that any additional water in the Martian crust and oxygen in surface silicates have not been part of this exchangeable system. Without more precise knowledge of the isotopic compositions of C and O in major Martian reservoirs and the size and nature of the near-surface reservoirs in equilibrium with the atmosphere, it is difficult to model in detail the extent of mass fractionation of these isotopes due to atmospheric loss.

6. Time Evolution of Radiogenic Components

Additional constraints on the evolution of Martian volatiles in time are provided by the distribution of the noble gas products from radioactive decay of ^{40}K, ^{129}I and ^{244}Pu. The 16 Myr half-life of extinct ^{129}I provides a chronometer for evolutionary events during the very earliest history, and a fundamental constraint is provided by the radiogenic ^{129}Xe content of the atmosphere. Based on estimates of 30 ppb for the global iodine content of Mars (Wänke and Dreibus, 1988), the ratio of radiogenic ^{129}Xe in the atmosphere to the total ^{127}I in Mars is around 10^{-7}. This provides a minimum estimate for $^{129}I/^{127}I$ at the time when a major global fractionation of iodine and xenon must have occurred and corresponds to a maximum interval of 160 Myr after the formation of the solar system ($^{129}I/^{127}I \sim 10^{-4}$). A further constraint on the details of this early fractionation is provided by the observation that $^{129}Xe/^{132}Xe$ for the interior component is indistinguishable from the solar value, within an uncertainty of around ± 0.02. In order to preserve the solar value, in the presence of 30 ppb iodine with an initial $^{129}I/^{127}I$ ratio $\sim 10^{-4}$, the initial concentration of ^{132}Xe in Mars must have been very high ($\geq 2 \times 10^{-7}$ ccSTP/g, based on the Chassigny data), comparable to the highest concentrations observed in some C-chondrites. If the isotopic composition of Chassigny xenon is typical of the Martian mantle, it is easy to calculate that the residual concentration of ^{132}Xe after the I-Xe fractionation would also have been substantial, between 10^{-7} and 10^{-10} cc/g depending on whether the fractionation was early or late.

Details of the I-Xe fractionation are unknown but are assumed to be a combination of outgassing, global melting, and the formation of a crust and depleted mantle. Specific models have been proposed in which the fractionation of xenon arose as a result of outgassing and differential solubility in a Martian hydrosphere (Musselwhite *et al.*, 1991), or based on differences in solubility of I and Xe in silicate melts during the process of outgassing (Musselwhite and Drake, 2000). In these models the large enrichment of ^{129}Xe in the atmosphere is achieved by a temporary storage of ^{129}I in the crust while the early atmosphere is drastically eroded and isotopically fractionated during hydrodynamic escape. The very low atmospheric abundance of fission xenon from the decay of extinct ^{244}Pu ($t_{1/2} = 82$ Myr) implies that a fractionation of Pu and I occurred while ^{244}Pu was 'live', and before escape of the hypothesized early dense atmosphere. It seems likely that this was part of the early global differentiation responsible for the I-Xe fractionation but it is not yet possible to add to the time constraints imposed by the ^{129}Xe excesses.

Argon-40 in the atmosphere provides clues to the more recent outgassing history of Mars. Mars contrasts with the Earth, where much higher ^{40}Ar atmospheric abundances result from extensive and continuous outgassing of the upper mantle. Based on estimates of ~ 500 ppm for the mean K abundance in Mars, the total amount of atmospheric ^{40}Ar represents less than 2% of that produced in the last 4.0 Gyr by radioactive decay of ^{40}K. This implies either very low rates of outgassing since the presumed loss of the early proto-atmosphere (Pepin, 1994), or

higher rates of outgassing combined with continuous loss by sputtering and impact erosion from the upper atmosphere (Scambos and Jakosky, 1990). Simple models involving degassing associated with partial melting, indicate a semi-quantitative consistency between the implied low outgassing rates of ^{40}Ar and the low rates of volcanism on Mars (e.g. Pepin, 1994; Greeley and Schneid, 1991).

Retention of significant primordial ^{36}Ar in the interior of Mars is implied by the recognition of an interior component with low $^{40}Ar/^{36}Ar$ ~200 (Mathew and Marti, 2001). The concentration of radiogenic ^{40}Ar resulting from 4.0 Gyr decay and a mean K concentration of 500 ppm is 3.2×10^{-5} ccSTP/g which would require a concentration of ^{36}Ar of ~10^{-7} cc/g to maintain $^{40}Ar/^{36}Ar$ below 300. This conclusion is consistent with the elemental ratios observed in Chassigny (^{36}Ar : ^{84}Kr : ^{132}Xe = 5 : 1 : 1; Mathew and Marti, 2001). However, such a high ^{36}Ar concentration contrasts with the terrestrial situation, where ^{36}Ar concentrations in the upper mantle are of the order of 10^{-10} cc/g. A conclusion that emerges from the above discussions is that Mars is a relatively undegassed planet in comparison to the Earth.

Direct evidence for changes in the isotopic composition of the Martian atmosphere comes from analyses of the meteorite ALH84001. Its Sm-Nd age of 4.5 Gyr (Nyquist *et al.*, 2001) indicates formation early in Mars history when ^{244}Pu was live, but after the decay of ^{129}I (Gilmour *et al.*, 1998). A major shock event at ~3.9 Gyr (Turner *et al.*, 1997) was probably responsible for incorporating ancient Martian atmospheric gases but the interior component could be a relict of its original crystallization. Marti and Mathew (2000) noted a relationship between nitrogen isotopic signatures and the $^{129}Xe/^{132}Xe$ ratio, which they proposed using as a time marker. These authors suggest that atmospheric nitrogen may have evolved from an initial light signature of $\delta^{15}N = -30‰$ to a value of $\delta^{15}N = 4 \pm 2‰$ at the time of gas implantation into ALH84001. This evolutionary model suggests that nitrogen was present in the atmosphere and was only slightly evolved, but that ~85% of the radiogenic ^{129}Xe had been released into the atmosphere at this time, or that subsequent release of primordial ^{132}Xe has kept almost in step with radiogenic ^{129}Xe. Further, since Chassigny and ALH84001 reveal identical light nitrogen ($\delta^{15}N = -30‰$) components, it appears that multiple reservoirs of volatiles with different nitrogen and radiogenic xenon signatures do exist in the Martian mantle and attest to limited exchanges between these reservoirs with the modern Martian atmosphere. A relevant aspect of the isotopic signature of the atmospheric Xe in ALH84001 is that it appears to show no fractionated characteristic of the modern atmosphere, and, apart from ^{129}Xe, still preserves a solar signature (Mathew and Marti, 2001). The time of incorporation, hence epoch, of the trapped atmospheric xenon into the nakhlites (formation ages of 1.3 Gyr) is less certain, although Gilmour *et al.* (2001) argue that it was introduced recently by mild shock associated with the ejection from Mars.

7. Overview and Implications

Information about the isotopic abundances of volatile elements on Mars derives from ground-based measurements, spacecraft instrumentation, and study of Martian meteorites in terrestrial laboratories. The major component in the Martian atmosphere is CO_2, followed by N_2 and ^{40}Ar. All other components are $\ll 1\%$. Several volatile species in the Martian atmosphere display strong isotopic fractionation, i.e., N and the noble gases, with the exception of Kr. Isotopic fractionation seen in Xe has been modeled to reflect massive and early loss of the atmosphere, which included total loss of all species save Xe. The atmosphere was later rejuvenated by internal degassing and possibly by addition of a late volatile-rich veneer. Isotopic fractionation seen in H, N, Ar and possibly Ne is explained by loss from this rejuvenated atmosphere over much longer geological times. Importantly, atmospheric Kr has very close to a solar composition and apparently has not been isotopically fractionated. The atmospheric D/H ratio is enriched over the mean terrestrial value by a factor of 5.5. Several models exist to explain various aspects of isotopic fractionation of atmospheric species, but the number of variables in these models is large, and thus we cannot be certain of their detailed applicability.

Most condensable volatiles are not expected to show appreciable isotopic fractionation effects from atmospheric loss. This is because of the existence of chemically exchangeable reservoirs on the Martian surface (e.g., the polar caps for H_2O and CO_2), which are much larger than the atmospheric reservoir for some species. Unfortunately, precise measurements of the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotopic ratios of atmospheric CO_2 do not yet exist. However, measurements of these ratios in secondary phases (e.g., carbonates, hydrated minerals, etc) in Martian meteorites show some significant isotopic variations of a few percent. Further, real differences exist in the $\delta^{17}O$ value between these secondary phases and silicates in the same meteorite. This difference implies that O in the Martian atmosphere and hydrosphere is not in chemical equilibrium with silicates or near-surface rocks. The D/H ratio in Martian meteorites shows significant variation from a low value of $\delta D = \sim 900\%o$ up to nearly the atmospheric value of $\delta D \cong 4200\%o$. This suggests that some secondary phases in these meteorites have exchanged with atmospheric H.

The noble gases and N in Martian meteorites also reveal one or more Martian interior components that are very different isotopically from the atmospheric one. Generally, this difference is a result of the large mass fractionation effects that have occurred in the atmospheric component. The interior component appears to have a solar composition for Xe and a $^{15}N/^{14}N$ ratio similar to that of enstatite meteorites. The isotopic composition of Ar in this interior component is poorly constrained, but is consistent with a solar composition. The existence of solar-like Xe in the Martian interior and solar-like Kr in the atmosphere strongly indicates that the heavier noble gases initially acquired by Mars had a solar composition, rather than compositions similar to those seen in primitive meteorites. However,

the elemental Ar/Kr/Xe ratios of this Martian interior component (as measured in Chassigny) are very strongly fractionated relative to solar compositions and are even more strongly fractionated than these elements in primitive meteorites. No good explanation exists for this contrast in elemental and isotopic fractionation, except possibly temperature-controlled adsorption.

Several isotopic ratios in the Martian atmosphere, e.g., D/H, ^{15}N/^{14}N, ^{36}Ar/^{38}Ar, ^{40}Ar/^{36}Ar, and ^{129}Xe/^{132}Xe, are expected to have evolved over part or all of Martian history due to atmospheric loss or addition of radiogenic components. In principle, if the time evolution of these isotopes could be documented, e.g. by measuring trapped gases in Martian meteorites or returned Martian rocks having different ages, much could be learned about the nature of the Martian atmosphere and crustal degassing throughout Martian history. In practice, however, an incomplete data base and the presence of interior volatile components in Martian meteorites complicate this evaluation.

Although the pressure of the Martian atmosphere is less than 1% that of the Earth's atmosphere, Martian volatiles show some similarities and some differences to those of Earth. Both planets likely had early fractionation loss of noble gases of solar-like composition. This may account for the similarity in the relative abundances of their Ar, Kr, and Xe, in spite of the large differences in elemental masses and absolute atmospheric abundances. Whether early Mars also was depleted in H_2O and CO_2 compared to the Earth is difficult to evaluate. The crust of the Earth obviously contains relatively large quantities of H_2O and of CO_2 in the form of carbonates. However, to the extent that Martian meteorites are representative of the Martian interior, Martian rocks are relatively poor in water. Further, spectroscopic measurements of Mars have yet to reveal any deposits of carbonate on the surface. Those isotopic fractionations measured in Martian meteorites suggest that the volatile reservoir involved in isotopic exchange with the Martian atmosphere is limited. Yet, the morphology of the Martian surface implies that early in its history Mars may have possessed abundant surface water (Masson *et al.*, 2001). All this suggests that Mars may contain a substantial quantity of interior volatiles, which have never outgassed into the atmosphere and which are not in isotopic exchange with the atmosphere. This would be consistent with the low (~2%) fractional degassing into the atmosphere implied for radiogenic ^{40}Ar. Part of the surface water on early Mars may now reside in the deeper crust.

However, it may also be the case that early Mars received more than one source of volatiles. The ratio of noble gases to C, N, and water is smaller by many orders of magnitude in primitive carbonaceous meteorites than in gas of solar composition. Thus, much of the water, C, and N on early Mars may have been added as a late carbonaceous veneer, possibly after loss of the early atmosphere. The ^{15}N/^{14}N ratio in the present atmosphere suggests that ~99% of the N has been lost to space, and it seems unlikely that a significant reservoir of N exists in the Martian surface. The C/N ratio of primitive meteorites is ~30 by weight, and the quantity of N_2 currently in the atmosphere is 1.4×10^{16} moles. Thus, we might deduce that late

addition of meteoritic volatiles would have added $\sim 8 \times 10^{19}$ moles of CO_2 to all of Mars. This is ~ 57 moles of CO_2 per cm^2 of the surface, which is equivalent to a layer of $CaCO_3$ ~ 20 meters thick. Even considering the likelihood that cratering in the first 1 Gyr of Martian history gardened and mixed the surface to depths of up to hundreds of meters (Hartmann *et al.*, 2001), this amount of $CaCO_3$ should, in principle, be observable from orbit using spectroscopic techniques. Either most of an early inventory of Martian carbon was deeply buried by basalt flows or cratering ejecta, or removed from the planet by impacts, or the predicted quantity of carbon on Mars, based on addition by a carbonaceous veneer and estimated amounts of nitrogen, is considerably too large.

The atmospheric abundance of ^{36}Ar also may not be consistent with the late meteorite veneer model. The $N/^{36}Ar$ ratio of primitive meteorites is $\sim 3 \times 10^6$ and the solar ratio is 28, whereas the $N/^{36}Ar$ ratio in the present Martian atmosphere is $\sim 6 \times 10^3$. Although large amounts of N and Ar have been lost from Mars, the $^{15}N/^{14}N$ and $^{38}Ar/^{36}Ar$ ratios suggest somewhat comparable fractions have been lost. Thus, if a late veneer of carbonaceous chondrite material was added to Mars, either the atmospheric loss of N has actually exceeded the loss of ^{36}Ar by orders of magnitude, or a significant surface reservoir exists for N (unlikely), or most of the ^{36}Ar in the atmosphere is a solar-derived component (contributing relatively little N) that has been degassed from the interior. A solar component of atmospheric Ar is consistent with the solar composition of atmospheric Kr. This consideration implies that most of the N and the noble gases on Mars had different origins.

We also can consider the possibility of addition of water to early Mars by a carbonaceous veneer. If early Mars had water to a global depth of at least 50 m, as suggested by some, this implies a water/C molar ratio of >5. Because primitive carbonaceous meteorites have C concentrations of several percent, this water/C ratio would require primitive meteorites to contain $\sim 20\%$ or more water, a value that is about a factor of two higher than water contents of carbonaceous chondrites. An alternative explanation may be that the late veneer added to Mars was even richer in volatiles, such as is the case with comets. Comets have measured C/N values greater than solar. Owen and Bar-Nun (1995a) suggested a cometary C/N ratio of 20 ± 10 a value not much different from that in carbonaceous chondrites. If we assume the solar C/N ratio of 4.9 as a lower limit and 99% loss of N over time, only ~ 3.3 m of $CaCO_3$ would be contained within the Martian surface. This smaller amount of carbonate should be easier to dilute by impact gardening of the surface. However, the C/O ratio in comets seems to be solar, and Owen and Bar-Nun (1995a) suggested an upper limit to the CO_2/H_2O ratio of 0.6. Thus, a postulated cometary source of volatiles would seem to require that substantial amounts of C be accreted to Mars in order to produce >50 m of water planet wide. It may be that water accreted to Mars was incorporated into the Martian surface prior to a time when atmospheric gases N_2, CO_2, and Ar were being significantly lost from the planet, e.g., by impact erosion of the atmosphere. Thus, a much

greater fraction of initial water may have been retained on Mars, compared to the remnants of these other gases that we observe today.

Finally, we point out that in spite of the considerable knowledge about the composition of Martian volatiles gained from the study of Martian meteorites, uncertainties remain. Is the noble gas component trapped in shergottite shock glass an accurate representation of the recent Martian atmosphere, or does it contain minor amounts of other components? How broadly representative of the Martian interior are the trapped N and noble gas components measured in Chassigny? Do the elementally fractionated Ar/Kr/Xe ratios observed in ALH84001 and the nakhlites represent fractionation of the recent Martian atmosphere during some simple absorption process? What has been the time evolution of the ^{129}Xe/^{132}Xe, ^{40}Ar/^{36}Ar, and ^{15}N/^{14}N ratios in the Martian atmosphere? What are the precise isotopic compositions of C and O in atmospheric volatiles, and with what surface reservoirs are these in isotopic equilibrium? Although we have presented above some reasonable answers to these questions, definitive answers may require study of Martian meteorites not yet found and precise, direct analyses of Martian volatiles, either in situ or in atmospheric and surface samples returned to Earth.

Acknowledgements

References

Acuña, M.H. *et al.*: 1998,'Magnetic Field and Plasma Observations at Mars: Initial Results of the Mars Global Surveyor Mission', *Science* **279**, 1676–1680.

Ahrens T. J.: 1990, 'Earth Accretion', *in* H.E. Newsom and J.H. Jones (eds.), *Origin of the Earth*, Oxford Univ. Press, New York, pp. 211–227.

Bao H., Thiemens, M.H., Farquhar, J., Campbell, D.A., Lee, C.C., Heine, K., and Loope, D.B.: 2000, 'Anomalous ^{17}O Compositions in Massive Sulphate Deposits on the Earth', *Nature* **406**, 176–178.

Becker, R.H., and Pepin, R.O.: 1984, 'The Case for a Martian Origin of the Shergottites: Nitrogen and Noble Gases in EETA79001', *Earth Planet. Sci. Lett.* **69**, 225–242.

Benz, W., and Cameron, A.G.W.: 1990, 'Terrestrial Effects of the Giant Impact', *in* H.E. Newsom and J.H. Jones (eds.), *Origin of the Earth*, Oxford Univ. Press, New York, pp. 61–67.

Bogard, D.D.: 1997, 'A Reappraisal of the Martian ^{36}Ar/^{38}Ar Ratio', *J. Geophys. Res.* **102**, 1653–1661.

Bogard, D.D. and Johnson, P.: 1983, 'Martian Gases in an Antarctic Meteorite', *Science* **221**, 651–654.

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., and Garrison, D.H.: 1999, 'Argon-39-argon-40 "Ages" and Trapped Argon in Martian Shergottites, Chassigny, and Allan Hills 84001', *Met. Planet Sci.* **34**, 451–473.

Bogard, D.D., Hörz, F., and Johnson, P.: 1986, 'Shock-implanted Noble Gases: An Experimental Study with Implications for the Origin of Martian Gases in Shergottite Meteorites', *J. Geophys. Res.* **91 suppl.**, 99–114.

Carr, M.H.: 1986, 'Mars: A water-rich Planet?', *Icarus* **68**, 187–216.

Carr, M.H.: 1996, *Water on Mars*, Oxford Univ. Press, New York.

Carr, M.H.: 1999, 'Retention of an Atmosphere on Early Mars', *J. Geophys. Res.* **104**, 21,897–21,909.

Clayton, R.N., and Mayeda, T.K.: 1984, 'The Oxygen Isotope Record in Murchison and Other Carbonaceous Chondrites', *Earth Planet. Sci. Lett.* **67**, 151–161.

Clayton, R.N., Mayeda, T.K., and Hurd, J.M.: 1974, 'Loss of Oxygen, Silicon, Sulfur and Potassium from the Lunar Regolith', *Geochim. Cosmochim. Acta Suppl.* **5**, 1801–1809.

Crider, D.H. *et al.*: 2000, 'Evidence of Electron Impact Ionization in the Magnetic Pile-up Boundary of Mars', *Geophys. Res. Lett.* **27**, 45–48.

Donahue, T.M.: 1986, 'Fractionation of Noble Gases by Thermal Escape from Accreting Planetesimals', *Icarus* **66**, 195–210.

Drake, M.J., Swindle, T.D., Owen, T., and Musselwhite, D.S.: 1994, 'Fractionated Martian Atmosphere in the Nakhlites?', *Meteoritics* **29**, 854–859.

Farquhar, J., Thiemens, M.H., and Jackson, T.: 1998, 'Atmosphere-surface Interactions on Mars: $\delta^{17}O$ Measurements of Carbonate from ALH 84001', *Science* **280**, 1580–1582.

Farquhar, J., Bao, H., and Thiemens, M.H.: 2000a, 'Atmospheric Influence of Earth's Earliest Sulfur Cycle', *Science* **289**, 756–758.

Farquhar, J., Savarino, J., Jackson, T.L. and Thiemens, M.H.: 2000b, 'Evidence of Atmospheric Sulphur in the Martian Regolith from Sulphur Isotopes in Meteorites', *Nature* **404**, 50–52.

Fox, J.L.: 1993, 'On the Escape of Oxygen and Hydrogen from Mars', *Geophys. Res. Lett.* **20**, 1847.

Fox, J.L.: 1997, 'Upper Limits to the Outflow of Ions at Mars: Implications for Atmospheric Evolution', *Geophys. Res. Lett.* **24**, 2901.

Fox, J.L., and Hac, A.: 1997, 'The $^{15}N/^{14}N$ Isotope Fractionation in Dissociative Recombination of N_2^+', *J. Geophys. Res.* **102**, 9191–9204.

Garrison, D.H., and Bogard, D.D.: 1998, 'Isotopic Composition of Trapped and Cosmogenic Noble Gases in Several Martian Meteorites', *Met. Planet. Sci.* **33**, 721–736.

Garrison, D.H., and Bogard, D.D.: 2000, 'Cosmogenic and Trapped Noble Gases in the Los Angeles Martian Meteorite', *Met. Planet. Sci.* **35**, A58 (abstract).

Geiss, J., and Reeves, H.: 1981, 'Deuterium in the Solar System', *Astron. Astrophys.* **93**, 189–199.

Gilmour, J.D., Whitby, J.A., and Turner, G.: 1998, 'Xenon Isotopes in Irradiated ALH84001: Evidence for Shock-induced Trapping of Ancient Martian Atmosphere', *Geochim. Cosmochim. Acta* **62**, 2555–2571.

Gilmour, J.D., Whitby, J.A., and Turner, G.: 1999, 'Martian Atmospheric Xenon Contents of Nakhla Mineral Separates: Implications for the Origin of Elemental Mass Fractionation', *Earth Planet. Sci. Lett.* **166**, 139–147.

Gilmour, J.D., Whitby, J.A., and Turner, G.: 2001, 'Disentangling Xenon Components in Nakhla: Martian Atmosphere, Spallation and Martian Interior', *Geochim. Cosmochim. Acta* **65**, 343–354.

Greeley, R.: 1987, 'Release of Juvenile Water on Mars: Estimated Amounts and Timing Associated with Volcanism', *Science* **236**, 1653–1654.

Greeley, R., and Schneid, B.D.: 1991, 'Magma Generation on Mars: Amounts, Rates and Comparisons with Earth, Moon and Venus', *Science* **254**, 996–998.

Greenwood, J.P., Riciputti, L.R. and McSween, H.Y., Jr.: 1997, 'Sulfide Isotopic Compositions in Shergottites and ALH 84001, and Possible Implications for Life on Mars', *Geochim. Cosmochim. Acta* **61**, 4449–4454.

Hartmann, W.K., Anguita, J., de la Casa, M.A., Berman, D.C., and Ryan, E.V.: 2001, 'Martian Impact Cratering 7: The Role of Impact Gardening', *Icarus* **149**, 37–53.

Holland, G., Lyon, I.C., Saxton, J.M., and Turner, G.: 2000, 'Very Low Oxygen-isotopic Ratios in Allan Hills 84001 Carbonates: a Possible Meteoritic Component?', *Met. Planet. Sci.* **35**, A76–A77.

Humayun, M., and Clayton, R.N.: 1995, 'Potassium Isotope Cosmochemistry: Genetic Implications of Volatile Element Depletion', *Geochim. Cosmochim. Acta* **59**, 2131–2148.

Hunten, D.M., Pepin, R.O., and Walker, J.C.G.: 1987, 'Mass Fractionation in Hydrodynamic Escape', *Icarus* **69**, 532–549.

Hutchins, K.S., and Jakosky, B.M.: 1996, 'Evolution of Martian Atmospheric Argon: Implications for Sources of Volatiles', *J. Geophys. Res.* **101**, 14,933–14,949.

Jakosky, B.M.: 1991, 'Mars Volatile Evolution: Evidence from Stable Isotopes', *Icarus* **94**, 14.

Jakosky, B.M.: 1993, 'Mars Volatile Evolution: Implications of the Recent Measurement of ^{17}O in Water from the SNC Meteorites', *Geophys. Res. Lett.* **20**, 1591–1594.

Jakosky, B.M., and Jones, J.H. : 1997, 'The History of Martian Volatiles', *Rev. Geophys.* **35**, 1–16.

Jakosky, B.M., Pepin, R.O., Johnson, R.E., and Fox, J.L.: 1994, 'Mars Atmospheric Loss and Isotopic Fractionation by Solar-wind-induced Sputtering and Photochemical Escape', *Icarus* **111**, 271–281.

Karlsson, H.R., Clayton, R.N., Gibson, E.K., Jr., and Mayeda, T.K.: 1992, 'Water in SNC Meteorites: Evidence for a Martian Hydrosphere', *Science* **255**, 1409–1411.

Kass, D.M., and Yung, Y.L.: 1995, 'Loss of Atmosphere from Mars due to Solar Wind-Induced Sputtering', *Science* **268**, 697.

Kent, A.J.R., Hutcheon, I.D., Ryerson, F.J., and Phinney, D.L.: 2001, 'The Temperature of Formaion of Carbonate in Martian Meteorite ALH84001: Constraints from Cation Diffusion', *Geochim. Cosmochim. Acta* **65**, 311–321.

Kieffer, H.H., Jakosky, B.M., and Snyder, C.W.: 1992, 'The Planet Mars: From Antiquity to the Present', *in* H.H. Kieffer, B.M. Jakosky, C.W. Snyder, and M.S. Matthews, (eds.), *Mars*, Univ. Arizona Press, Tucson, pp. 1–33.

Krasnopolsky, V.A., Bjoraker, G.L., Mumma, M.J., and Jennings, D.E.: 1997, 'High Resolution Spectroscopy of Mars at 3.7 and 8 μm : A Sensitive Search for H_2O_2, H_2CO, HCl and CH_4, and Detection of HDO', *J. Geophys. Res.* **102**, 6524–6534.

Lammer, H., and Bauer, S.J.: 1991, 'Non-thermal Atmospheric Escape from Mars and Titan', *J. Geophys. Res.* **96**, 1819.

Leshin, L.A.: 2000, 'Insights into Martian Water Reservoirs from Analysis of Martian Meteorite QUE 94201', *Geophys. Res. Lett.* **27**, 2017–2020.

Leshin, L.A., Epstein, S., and Stolper, E.M.: 1996, 'Hydrogen Isotope Geochemistry of SNC Meteorites', *Geochim. Cosmochim. Acta* **60**, 2635–2650.

Leshin, L.A., McKeegan, K.D., Carpenter, P.K., and Harvey R.P.: 1998, 'Oxygen Isotopic Constraints on the Genesis of Carbonates from Martian Meteorite ALH 84001', *Geochim. Cosmochim. Acta* **62**, 3–13.

Luhman, J.G.: 1997, 'Correction to "The Ancient Oxygen Exosphere of Mars: Implications for Atmosphere Evolution", by Zhang *et al.*, *J. Geophys. Res.* **102**, 1637.

Luhmann, J.G., Johnson, R.E., and Zhang, M.H.G.: 1992, 'Evolutionary Impact of Sputtering of the Martian Atmosphere by O^+ Pick-up Ions', *Geophys. Res. Lett.* **19**, 2151.

Lundin, R., *et al.*: 1989, 'First Measurements of the Ionsphere Plasma Escape from Mars', *Nature* **341**, 609.

Lundin, R., *et al.*: 1990, 'Aspera/Phobos Measurements of the Ion Outflow from the Martian Atmosphere', *Geophys. Res. Lett.* **17**, 873–876.

Marti, K., and Mathew, K.J.: 2000, 'Ancient Martian Nitrogen', *Geophys. Res. Lett.* **27**, 1463–1466.

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.

Masson, P., Carr, M.H., Costard, F., Greeley, R., Hauber, E., and Jaumann, R.: 2001, 'Geomorphologic Evidence for Liquid Water', *Space Sci. Rev.*, this volume.

Mathew, K.J., and Marti, K.: 2001, 'Early Evolution of Martian Volatiles: Nitrogen and Noble Gas Components in ALH84001 and Chassigny', *J. Geophys. Res.*, **106**, 1401–1422.

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', *Met. Planet. Sci.* **33**, 655–664.

McElroy, M.B., Kong, T.Y., Yung, Y.L., and Nier, A.O.: 1976, 'Composition and Structure of the Martian Upper Atmosphere. Analysis of Results from Viking', *Science*, **194**, 1295–1298.

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.: 1985, 'SNC Meteorites: Clues to Martian Petrologic Evolution?' *Rev. Geophys.* **23**, 391–416.

Meier, R., and Owen, T.: 1999, 'Cometary Deuterium', *Space Sci. Rev.* **90**, 33–43.

Melosh, H.J., and Vickery, A.M.: 1989, 'Impact Erosion of the Primordial Atmosphere of Mars', *Nature* **338**, 487–489.

Mittlefehldt, D.W.: 1994, 'ALH84001, a Cumulate Orthopyroxenite Member of the Martian Meteorite Clan', *Meteoritics* **29**, 214–221.

Miura, Y.N., Nagao, K., Sugiura, N., Sagawa, H., and Matsubara, K.: 1995, 'Orthopyroxene ALH84001 and Shergottite ALH7705: Additional Evidence for a Martian Origin from Noble Gases', *Geochim. Cosmochim. Acta* **59**, 2105–2113.

Mohapatra, R.K., and Ott, U.: 2000, 'Trapped Noble Gases in Sayh al Uhaymir 005: A new Martian Meteorite from Oman', *Met. Planet. Sci.* **35**, A113 (abstract).

Murty, S.V.S., and Mohapatra, R.K.,: 1997, 'Nitrogen and Heavy Noble Gases in ALH84001: Signature of Ancient Martian Atmosphere', *Geochim. Cosmochim. Acta* **61**, 5417–5428.

Musselwhite, D.S., and Drake, M.J.: 2000, 'Early Outgassing of Mars: Implications from Experimentally Determined Solubility of Iodine in Silicate Magmas', *Icarus* **148**, 160–175.

Musselwhite, D.M., Drake, M.J., and Swindle, T.D.: 1991, 'Early Outgassing of Mars Supported by Differential Water Solubility of Iodine and Xenon', *Nature* **352**, 697–699.

Nier, A., and McElroy, M.B.: 1977, 'Composition and Structure of Mars' Upper Atmosphere: Results from the Neutral Mass Spectrometers at Viking 1 and 2', *J. Geophys. Res.* **82**, 4341–4350.

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.

Nyquist, L.E., Bogard, D.D., Shih, C.-Y., Greshake, A., Stöffler, D., and Eugster, O.: 2001, 'Ages and Geologic Histories of Martian Meteorites', *Space Sci. Rev.*, this volume.

Ohmoto, H.: 1986, 'Stable Isotope Geochemistry of Ore Deposits', *in* J.W. Valley, H.P. Taylor, J.R. O'Neil (eds.), *Stable Isotopes in High Temperature Geological Processes*, *Rev. Mineral.* **16**, Mineral. Soc. Am., Washington, pp. 491–560.

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.

Owen, T.: 1992, 'The Composition and Early History of the Atmosphere of Mars', *in* H.H. Kieffer *et al.*, *Mars*, Univ. Arizona Press, Tucson, pp. 818–834.

Owen, T.: 1997, 'From Planetesimals to Planets: Contributions of Icy Planetesimals to Planetary Atmospheres', *in* Y.J. Pendleton and A.G.G.M. Tielens (eds.), *From Stardust to Planetesimals*, Astron. Soc. Pac. Conf. Ser. **122**, 435–450.

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* AIP Conf. Proc. **34**, pp. 123–128.

Owen, T., and Bar-Nun, A.: 1998, 'From the Interstellar Medium to Planetary Atmospheres via Comets', *Chemistry and Physics of Molecules and Grains in Space*, Faraday Discussions **109**, Roy. Soc. Chem., London, p. 453.

Owen, T., and Bar-Nun, A.: 2000, 'Volatile Contributions from Icy Planetesimals', *in* R. Canup and K. Righter (eds.), *Origin of the Earth and Moon*, Univ. Arizona Press, pp. 459–471.

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., Maillard, J.P., de Bergh, C., and Lutz, B.L.: 1988, *Science* **240**, 1767.

Ozima, N., and Podosek, F.A.: 1983, *Noble Gas Geochemistry*, Cambridge Univ. Press, 367 pp.

Pepin, R.O.: 1991, 'On the Origin and Early Evolution of Terrestrial Planet Atmospheres and Meteoritic Volatiles', *Icarus* **92**, 2–79.

Pepin, R.O.: 1994, 'Evolution of the Martian Atmosphere', *Icarus* **111**, 289–304.

Pepin, R.O.: 1997, 'Evolution of Earth's Noble Gases: Consequences of Assuming Hydrodynamic Loss Driven by Giant Impact', *Icarus* **126**, 148–156.

Pepin, R.O., Becker, R.H., and Rider, P.E.: 1995, 'Xenon and Krypton Isotopes in Extraterrestrial Regolith Soils and in the Solar Wind', *Geochim. Cosmochim. Acta* **59**, 4997–5022.

Porcelli, D., and Wasserburg, G.J.: 1995, 'Mass Transfer of Xenon through a Steady-state Upper Mantle', *Geochim. Cosmochim. Acta* **59**, 1991–2007.

Rieder, R., Economou, T., Wänke, H., Turkevich, A., Crisp, J., Brückner, J., Dreibus, G. and Mc-Sween, H.Y.: 1997, 'The Chemical Compositions of Martian Soil and Rocks returned by the mobile Alpha Proton X-ray Spectrometer: Preliminary Results from the X-ray Mode', *Science* **278**, 1771–1774.

Robert, F., and Epstein, S.: 1982, 'The Concentration and Isotopic Composition of Hydrogen, Carbon, and Nitrogen in Carbonaceous Chondrites', *Geochim. Cosmochim. Acta* **46**, 81–95.

Romanek, C.S., Grady, M.M., Wright, I.P., Mittlefehldt, D.W., Socki, R.A., Pillinger, C.T., and Gibson, E.K., Jr.: 1994, 'Record of Fluid-rock Interactions on Mars from the Meteorite ALH 84001', *Nature* **372**, 655–657.

Saxton, J.M., Lyon, I.C., and Turner, G.: 1998, 'Correlated Chemical and Isotopic Zoning in Carbonates in the Martian Meteorite ALH84001', *Earth Planet. Sci. Lett.* **160**, 811–822.

Scambos, T.A., and Jakosky, B.M.: 1990, 'An Outgassing Release Factor for Nonradiogenic Volatiles on Mars', *J. Geophys. Res.* **95**, 14,779–14,787.

Schubert, G., and Spohn, T.: 1990, 'Thermal History of Mars and the Sulfur Content of its Core', *J. Geophys. Res.* **95**, 14,095–14,104.

Shearer, C.K., Layne, G.D., Papike, J.J., and Spilde, M.N.: 1996, 'Sulfur Isotope Systematics in Alteration Assemblages in Martian Meteorite Allan Hills 84001', *Geochim. Cosmochim. Acta* **60**, 2921–2928.

Shukolyukov, Y.A., Nazarov, M.A., and Schultz, L.: 2000, 'Dhofar 019: A Shergottite with an Approximate 20-million-year Exposure Age', *Met. Planet Sci.* **35**, A147 (abstract).

Swindle, T.D., and Jones, J.H.: 1997, 'The Xenon Isotopic Composition of the Primordial Martian Atmosphere: Contributions from Solar and Fission Components', *J. Geophys. Res.* **102**, 1671–1678.

Swindle, T.D., Caffee, M.W., and Hohenberg, C.M.: 1986, 'Xenon and Other Noble Gases in Shergottites', *Geochim. Cosmochim. Acta* **50**, 1001–1015.

Swindle, T.D., Grier, J.A., and Burkland, M.K.: 1995, 'Noble Gases in Orthopyroxenite ALH84001: A Different Kind of Martian Meteorite with an Atmospheric Signature', *Geochim. Cosmochim. Acta* **59**, 793–801.

Terribilini, D., Eugster, O., Burger, M., Jakob, A., and Krähenbühl, U.: 1998, 'Noble Gases and Chemical Composition of Shergotty Mineral Fractions, Chassigny, and Yamato 793605: The Trapped Argon-40/argon-36 Ratio and Ejection Times of Martian Meteorites', *Met. Planet Sci.* **33**, 677–684.

Thiemens, M.H., Jackson, T.L., and Brenninkmeijer, C.A.M.: 1995, 'Observation of a Mass Independent Oxygen Isotopic Composition in Terrestrial Atmospheric CO_2, the Link to Ozone Chemistry, and the Possible Occurrence in the Martian Atmosphere', *Geophys. Res. Lett.* **22**, 255–257.

Treiman, A.H., Gleason, J.D., and Bogard, D.D.: 2000, 'The SNC Meteorites are from Mars', *Planet. Space Sci.* **48**, 1213–1230.

Turner, G., Knott, S.F., Ash, R.D., and Gilmour, J.D.: 1997, 'Ar-Ar Chronology of the Martian Meteorite ALH84001: Evidence for the Timing of the Early Bombardment of Mars', *Geochim. Cosmochim. Acta* **61**, 3835–3850.

Valley, J.W., Eiler, J.M., Graham, C.M., Gibson, E.K., Romanek, C.S. and Stolper, E.M.: 1997, 'Low-temperature Carbonate Concretions in the Martian Meteorite ALH 84001: Evidence from Stable Isotopes and Mineralogy', *Science* **275**, 1633–1638.

Wänke, H., and Dreibus, G.: 1988, 'Chemical Compositions and Accretion History of Terrestrial Planets', *Phil. Trans. Roy. Soc. Lond.* **A325**, 545–557.

Watson, L.L., Hutcheon, J.D., Epstein, S. 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.

Wiens, R.C.: 1988, 'Noble Gases Released by Vacuum Crushing of EETA79001 Glass', *Earth Planet. Sci. Lett.* **91**, 55–65.

Wiens, R.C., and Pepin, R.O.: 1988, 'Laboratory Shock Emplacement of Noble Gases, Nitrogen, and Carbon Dioxide into Basalt, and Implications for Trapped Gases in Shergottite EETA79001', *Geochim. Cosmochim. Acta* **52**, 295–307.

Wiens, R.C., Becker, R.H., and Pepin, R.O.: 1986, 'The Case for a Martian Origin of the Shergottites, II. Trapped and Indigeneous Gas Components in EETA79001 Glass', *Earth Planet Sci. Lett.* **77**, 149–158.

Yung, Y.L., Wen, J.S., Pinto, J.P., Allen, M., Pierce, K., and Paulom, S.: 1988, 'HDO in the Martian Atmosphere: Implications for the Abundance of Crustal Water', *Icarus* **76**, 146.

Zakharov, A.V.: 1992, 'The Plasma Environment of Mars: Phobos Mission Results', *AGU Geophys. Monograph* **66**, 327.

Zhang, M.H.G., Luhmann, G., Bougher, S.W., and Nagy, A.F.J.: 1993, 'The Ancient Oxygen Exosphere of Mars: Implications for Atmospheric Evolution', *Geophys. Res.* **98**, 10915.

Zipfel, J., Scherer, P., Spettel, B., Dreibus, G., and Schultz, L.: 2000, 'Petrology and Chemistry of the new Shergottite Dar al Gani 476', *Met. Planet. Sci.* **35**, 95–106.

Address for offprints: Planetary Sciences SN, NASA Johnson Space Center, Houston, TX 77058, USA, (donald.d.bogard1@jsc.nasa.gov)